STUDIES ON ADSORPTION & FLOTATION CHARACTERISTICS OF BEACH SAND MINERALS

BY

SHARAD GOVIND DIXIT

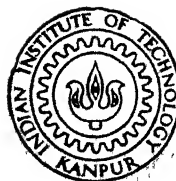DEPARTMENT OF METALLURGICAL ENGINEERING
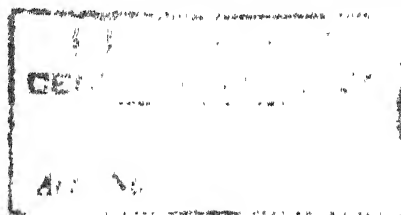## INDIAN INSTITUTE OF TECHNOLOGY KANPUR
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STUDIES ON ADSORPTION AND FLOTATION CHARACTERISTICS

OF

BEACH SAND MINERALS

A thesis submitted

In Partial fulfilment of the requirements

for the Degree of

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by

Sharad Govind Dixit

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CERTIFICATE

Certified that the work presented in this thesis has been carried out by S.G. Dixit under my supervision and has not been submitted elsewhere for a degree.

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C O N T E N T S

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LIST OF SYMBOLS

K_h	-	Hydrolysis Constant of Sodium Oleate
S	-	Actual Concentration of Sodium Oleate
Θ	-	Degree of Hydrolysis of Na-Oleate
pH	-	$-\log C_{H^+}$
Γ	-	Adsorption per gram of the mineral
Γ'	-	The expression $K_1 C_{Ol^-}^{n_1}$
V	-	Volume of the Solution
$C_{L_{X^-}}$	-	Concentration of the Collector anion X^- in liquid phase
$C_{L_{OH^-}}$	-	Concentration of OH^- ions in liquid phase
$C_{S_{X^-}}$	-	Concentration of Collector anion X^- at the surface
$C_{S_{OH^-}}$	-	Concentration of OH^- ions at the surface
z	-	Valency of the anion
R	-	Gas Constant
T	-	Temperature
L_{MX_2}	-	Solubility Product at the Solid-Liquid Interface of MX_2
L_{MOH_2}	-	Solubility Product of MOH_2 at the Solid-Liquid Interface
F	-	Faraday Constant
a	-	Activity
ν	-	Surface Free Energy
Γ_{X^-}	-	Surface Excess of X^- ions
Γ_{OH^-}	-	Surface Excess of OH^- ions
f	-	Activity Coefficient
E_o, E, E_1	-	Electrode Potentials

C_{H^+} , C_{HOl} , C_{OH^-} , C_{Ol^-} — Concentrations of the species at the subscript

K_o , K_c , K_c' , K_d , K_F — Equilibrium Reaction Constants

K_1 , n_1 , K_2 , n_2 , K_2' , m — Constants

$\triangle F_I$, $\triangle F_{II}$ — Free Energy Change of the Reactions

P, q, P, Q, a, b, a_1 , b_1 , m' — Constants

Subscripts

m   stands for micelle

L, s   stand for solution phase

S   stands for surface phase

( ) and $\underline{\big[\quad \big]}$ denote concentration terms.

SYNOPSIS

STUDIES ON ADSORPTION AND FLOTATION CHARACTERISTICS
OF BEACH SAND MINERALS, a thesis submitted in partial
fulfilment of the requirements of the degree of
M.Tech. in Metallurgical Engineering by Sharad Govind
Dixit to the Department of Metallurgical Engineering,
Indian Institute of Technology, Kanpur in December 1967.

The investigations on the flotation and adsorption
characteristics of the three important constituents of the beach
sand, namely, ilmenite, monazite and zircon are reported in this
presentation.

Chapter I includes a general survey of the beneficiation
of the monazite sand minerals with special reference to the
investigations into their beneficiation by froth flotation. The
dependence of the process on several physico-chemical parameters,
such as adsorption, is clearly brought out and it is indicated
that much remains to be done to unravel precisely the effects of
these parameters.

In Chapter II, the specifications of the chemicals and
minerals used are described as also a method for the estimation
of Na-oleate.

In Chapter III, experimental procedures are described in
details and the experimental results are reported on the variation
of flotation and adsorption with pH in case of ilmenite, monazite
and zircon.

The discussion of the experimental results is included
Chapter IV. It is concluded that there exists an experimental

correlation between flotation and adsorption magnitudes. On the basis of ionic equilibrium considerations it is found that the adsorption magnitude depends on C_{Ol-} and C_{OH-}/C_{Ol-} . A quantitative relationship is worked out. It is found to be reasonably satisfactory.

Chapter V deals with the role of OH^- ion as a depressor. The discussion is mainly aimed at critically examining the validity of the Barsky's law which is based on the competition between OH^- ion and collector anion for adsorption on the mineral surface. The problem is considered in a much wider context and does not exclusively pertain to any specific systems such as monazite sand minerals. It is maintained that modified Barsky's law may be valid if either constancy of adsorption magnitude or surface free energy along the contact curve indicating flotation / no flotation transition is proved.

Chapter VI summarises the conclusions arrived at and indicates some avenues for future research work in the field.

INTRODUCTION

In recent years there has been a growing tendency to incorporate flotation based beneficiation circuits for upgrading the valuable minerals. This has been witnessed in the beneficiation of beach sand minerals also, though conventionally, electrostatic and magnetic separation units are used on a large scale. For example, in 1960, in U.S.A. four plants were working on concentration of ilmenite, one of the constituents of beach sand deposits; and 617,300 tons of ore treated to produce 274,875 tons of concentrate (1). In Australia, there are plants which have mixed circuits with flotation, magnetic and electrostatic units (e.g., The Zircon Rutile Ltd., Australia(2)). Froth flotation is essentially a process, which taking advantage of the selective behaviour of the different conditioned mineral surfaces towards air bubbles sticking to the surfaces, effects upgrading of the minerals in the most efficient manner. The encouraging industrial trend has initiated large scale research on the flotation characteristics of the beach sand minerals; particularly in Russia and of late in India.

1.1 **BEACH SAND DEPOSITS IN INDIA:** In 1909 Schomberg(3), a German national, discovered the monazite deposits of Travancore. The deposit proved to be twice as rich in thorium content as compared to the Brazilian monazite. The belt starting from Cape Comorin to Kayamkulam and spreading over hundred miles is by far the largest source of high grade ilmenite, zircon, rutile and

monazite in the world(4).   There are several other deposits.

1.2 <u>BEACH SAND MINERALS</u>:   The black sand contains valuable
and strategic minerals like monazite (Ce, Dy, Nd)PO_4 ilmenite
$FeTiO_3$, zircon $ZrSiO_4$, rutile TiO_2, sillimnite Al_2SiO_5,
quartz SiO_2 and some garnet and hornblende.   Typical composition
of the beach sands of Travancore is reported to be as follows(5).

<div align="center">

Ilmenite 75-80%, Zircon 4-6%, Rutile 3-6%

Sillimnite 2-5%, Monazite 1-1.5%, Silica

4-7% and traces of Hornblende and Garnet.

</div>

Size analysis and minerological descriptions of the
minerals and other pertinent information is given in Appendix A.

1.3 <u>BENEFICIATION OF THE BEACH SANDS BY FROTH FLOTATION</u>:
Selective flotation of the beach sand constituents
has been reported by many workers.

In 1934, in Australia zircon was separated with soap
solution(6).   In 1935, D.J. Burke(7) gave a flotation scheme
to separate constituents of the sand minerals using soap
solution.   In 1939, W.R. Poole(8) gave a scheme of beneficiation
in which flotation was recommended to separate zircon from
rutile and ilmenite.   G. Gutzeit and P. Kovalive(9) in 1939
introduced sodium silicate as a depressor in the flotation of
the beach sand minerals.   They used potassium palmitate and
dodecylsulfonate as collectors.   In 1943, D.S. Phelp(10) used
wood creosote and a sodium sulphonated mineral oil as collectors.
In 1945, R.A. Pickens(11) reported ilmenite separation from
rutile using 0.06 lbs/ton of pine oil and 0.2 lb/ton of the

reaction product of thiourea and β-chloroethyloleate. In 1952
R.E. Cuthburtson(12) used cationic amine acetates and starch
to separate monazite from heavy minerals like rutile. In 1960,
G.V. Subramanya(13) suggested an alkaline circuit (pH 11.5)
instead of usual acid circuit. Sodium oleate and sodium stearate
mixture was used as a collector.

In 1958, I.N. Plaksin and E.M. Chapligina(14) studied
the influence of oxygen and nitrogen on separation by flotation
of titanium and zirconium minerals. It was shown that the oxygen
activates the flotation of these minerals. In 1962, I.N. Plaksin
et.al(15) investigated the action of sodium fluosilicate as
depressor for monazite etc. In 1963, I.N. Plaksin and
S.N. Dorokhina(16) studied the mechanism of the action of oxidised
oleic acid on the selective flotation of titano-zirconium sands.
In 1964, I.N. Plaksin et.al(17) studied the influence of halide
ions on emulsified oleic acid flotation of titano-zirconium sands.
In 1965, I.N. Plaksin and coworkers(18) investigated the chemical
mechanism of the controlling action of sodium fluosilicate using
I.R. spectroscopy.

In India work was done on sand deposits from Travancore.

In 1955, Nayak(19) investigated the flotation
behaviour of the minerals using oleic acid as collector and
alizarin red-S as depressant.

In 1959, K.M. Pai, R. Mallikarjunan and A.A. Krishnan(20)
studied the flotation behaviour of these minerals using sodium
linoleate and linolenate as collectors and sodium silicate as
depressors.

In 1965, K.K. Majumdar et.al(21) studied the conditions for selective flotation of beach sand monazite using sodium oleate as the collector and sodium silicate as depressor. Also, T.R. Madhavan et.al(22) investigated selective flotation of sillimnite, zircon and rutile.

The above studies reveal that:

1) all the mineral constituents of the beach sand are floated efficiently by fatty acid collectors;

2) very little selectivity is obtained if only fatty acids are used, and sometimes proper adjustment of pH may give separation;

3) the quantity of collector that is sufficient to cause 100% recovery at a favourable pH is about 150 - 200 mg/litre for 15 to 20% slurry;

4) sodium silicate causes depression of rutile, ilmenite and zircon markedly, while garnet and monazite are depressed to a lesser extent;

5) selective flotation of each constituent should be possible under suitable conditions.

1.4 PHYSICO-CHEMICAL FACTORS AFFECTING FLOTATION OF THE MINERALS:

Separation of solids by flotation is characterised by the establishment of contact among three phases. These three phases are: solid to be floated, an aqueous electrolyte solution and gas. To gain an understanding of the flotation system, it is therefore essential to study the chemical and physical properties of the interfaces established and to elucidate the effect of changes in composition of the bulk phases on the interfaces. The

flotation is essentially dependent on the magnitude of adsorption
of the collector on to the mineral surface. This in turn is
dependent on the nature of the mineral surface and ionic condition
of the aqueous solution. pH of the solution has a marked effect
on the adsorption of collector ions and hence flotation.

The chemisorption of the soap collectors from aqueous
media at the solid-liquid interface has been the subject of
many investigations. Mention may be made of a few important
attempts to elucidate the mechanism of the adsorption or to
correlate this with flotation. It has been found that flotation
involving soaps as collectors proceeds best when the fractional
coverage,θ,is much less than unity(23). This means that mostly
a partial monolayer coverage is sufficient to cause efficient
flotation. On the basis of ζ -potential and coagulation
measurements, Ottewill and Watanabe(24) have shown that anionic
collectors are adsorbed on positive sites on a surface.

D.W. Fuerstenau(25) in 1957 showed in case of quartz-
dodecylammoniumacetate system that there is experimental correlation
between adsorption and flotation.

However, there seems to be very little work done on
the correlation between adsorption of anionic soap collectors
and flotation. A.S. Peck(26) in 1963 reported the mechanism
of adsorption of oleic acid on barite as the pH changes.

As far as monazite sand minerals are concerned no work
has been reported on the adsorption of the anionic soap collectors
on to the mineral surfaces, the change of adsorption with pH,
the mechanism of adsorption and correlation between the adsorption

and the flotation characteristics.

1.5 <u>STATEMENT OF THE PROBLEM:</u> In view of the increasing scope
of the flotation studies of beach sand minerals by anionic soap
collectors, such as sodium oleate, it is desirable to understand
the adsorption behaviour of these sand minerals towards soap
collectors and to seek for correlation between adsorption and
flotation, if any. It would be also interesting to know how
the different physico-chemical factors affect the adsorption and
flotation behaviour. In particular, the role of H^+ and OH^-
ions are worth studying. The effect of pH in alkaline region,
particularly its quantitative aspects is a matter worthy of
investigation. The controversy boils down to the theoretical
validity of Barsky's [27] empirical postulate which is based on
competition of collector anion and depressor hydroxyl ion for
adsorption on to the solid surface (see Chapter - V).

In the present work, results of investigation on the
following topics together with accompanying discussions and
conclusions, are being presented:

    (1)   parallel adsorption and flotation studies on
some monazite sand minerals

    (2)   correlation of the parallel studies with
specific reference to variation of pH and
derivation of a quantitative relationship

    (3)   examination of theoretical validity of Barsky's Law.

CHAPTER - II

CHEMICALS AND MINERALS

In the present work aimed at studying adsorption and flotation of the beach sand minerals, ilmenite, monazite and zircon have been selected as these represent three important groups of minerals, namely, oxide, phosphate and silicate respectively.

The collector used for the flotation experiments was sodium oleate ($C_{17}H_{33}COONa$). The details of the chemicals and the mineral samples used are mentioned below.

2.1 CHEMICALS:

Dowfroth-250:- Dowfroth-250 is the first water soluble frother introduced by Tveter(28) in 1952 through the Dow Chemical Company. This is a low viscocity liquid soluble in water and can be represented by the following general formula:

$$CH_3 - (O-C_3H_6)_n -OH_6$$
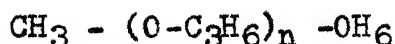
In fact it is not a single chemical entity. It consists of a mixture of homologues of varying molecular weights. The reagent is soluble in water and is effective as a frother even at low concentrations. Some of the physical properties are listed in Table 1(29).

This reagent was used as a frother in all the flotation experiments.

TABLE 1

Properties of Dowfroth-250	
Avg. Mol. wt.	250
Sp. gr. at 25 $^\circ$C	0.976
Viscosity at 25 $^\circ$C in centipoise	10.2
Boiling point $^\circ$C	252
Freezing point $^\circ$C	-71
Flash point $^\circ$F	285

Oleic Acid:- The sample of oleic acid was obtained from Hormel Institute, University of Minnesota. It was prepared from olive oil by low temperature fractional crystallisation and high vacuum fractional distillation. Estimated purity was greater than 99% by gas-liquid and thin layer chromatography analysis. Iodine value was 89.9 and diene conjugation 0.03 per cent. This sample was used for the preparation of sodium oleate.

2.2 PREPARATION OF SODIUM OLEATE(30): Equivalent amounts of oleic acid and annalar sodium hydroxide were transferred to a round bottomed flask and ethyl alchohol (50 cc) was added. The ethyl alchohol used was distilled twice and then kept overnight with quicklime and redistilled. The whole mass was refluxed over a water bath for about one hour. Subsequently excess alchohol was removed by evaporation and the syrupy mass was poured hot in acetone which was distilled after keeping overnight with $CaCl_2$. Sodium oleate thus precipitated was filtered and washed with acetone. The dried powder was stored in dessicator.

2.3 COLORIMETRIC ESTIMATION OF SODIUM OLEATE: For determining

the adsorption magnitude of the collector on to the mineral surface, a method of estimation of sodium oleate (the collector used in the present work) quantitatively was necessary. A colorimetric method was perfected for the estimation of the soap using nile blue as the colour developing indicator.

R. Goffin(31) in 1948 studied the colour reactions of higher fatty acids. He reported that the sulphate or chloride of nile blue produced a blue colour with soaps. At pH 12 the nile blue turns red but in the presence of soaps such as the oleates a complex is formed which shifts the point of colour change to higher pH. Based on this, R. Goffin and M. Conchoud(32) developed a method of colorimetric estimation of unsaturated fatty acids using sodium carbonate for adjusting pH and sodium aliginate. Filter photometer with yellow filters was used for measurement of the absorbance.

In the present studies the conditions of the adsorption experiments were almost identical with flotation experiments and hence use of sodium hydroxide was made for pH adjustment. It was therefore possible to make use of the above mentioned colour reaction for colorimetric estimation of sodium oleate. Since sodium hydroxide is a strong alkali, there are serious changes in pH and hence the need to buffer the solution. This was done with the help of di-sodium hydrogen phosphate.

Sodium oleate prepared by the method stated earlier was used for constructing a standard curve. The absorbance and percent transmittance were measured on spectronic-20 colorimeter.

The pH of the solution was maintained at 11.1 by adding 50 ml of 0.05M di-sodium hydrogen phosphate solution and 5.1 ml of 0.1M sodium hydroxide solution. 4 ml of 0.01% nile blue solution was used for the development of the colour. The volume of the solution was made upto 100 ml with buffer at pH 11.1 and then percent transmittance or absorbance was measured.

Figure 1 shows the variation of absorbance for various wavelengths and for two different concentrations of sodium oleate. It is found that maximum absorbance is obtained around 615 mμ. Thus, this was considered as the proper wavelength for estimation.

Figure 2 gives the standard curve (615 mμ, pH 11.1 and 4 ml of 0.01% nile blue addition). The straight line passing through the origin proves that Beer's law is obeyed.

This method is very much sensitive to pH changes; hence pH should be constant.

Time required for the development of the colour is short and measurements should be made within 5 - 10 minutes of the addition of nile blue.

Excess of Cl^- ions inhibit the colour production and should be avoided.

Any change due to turbidity should be corrected for by having suitable blanks.

With this, the accuracy of the method becomes appreciable and 10^{-6} mols per litre of sodium oleate can be detected.
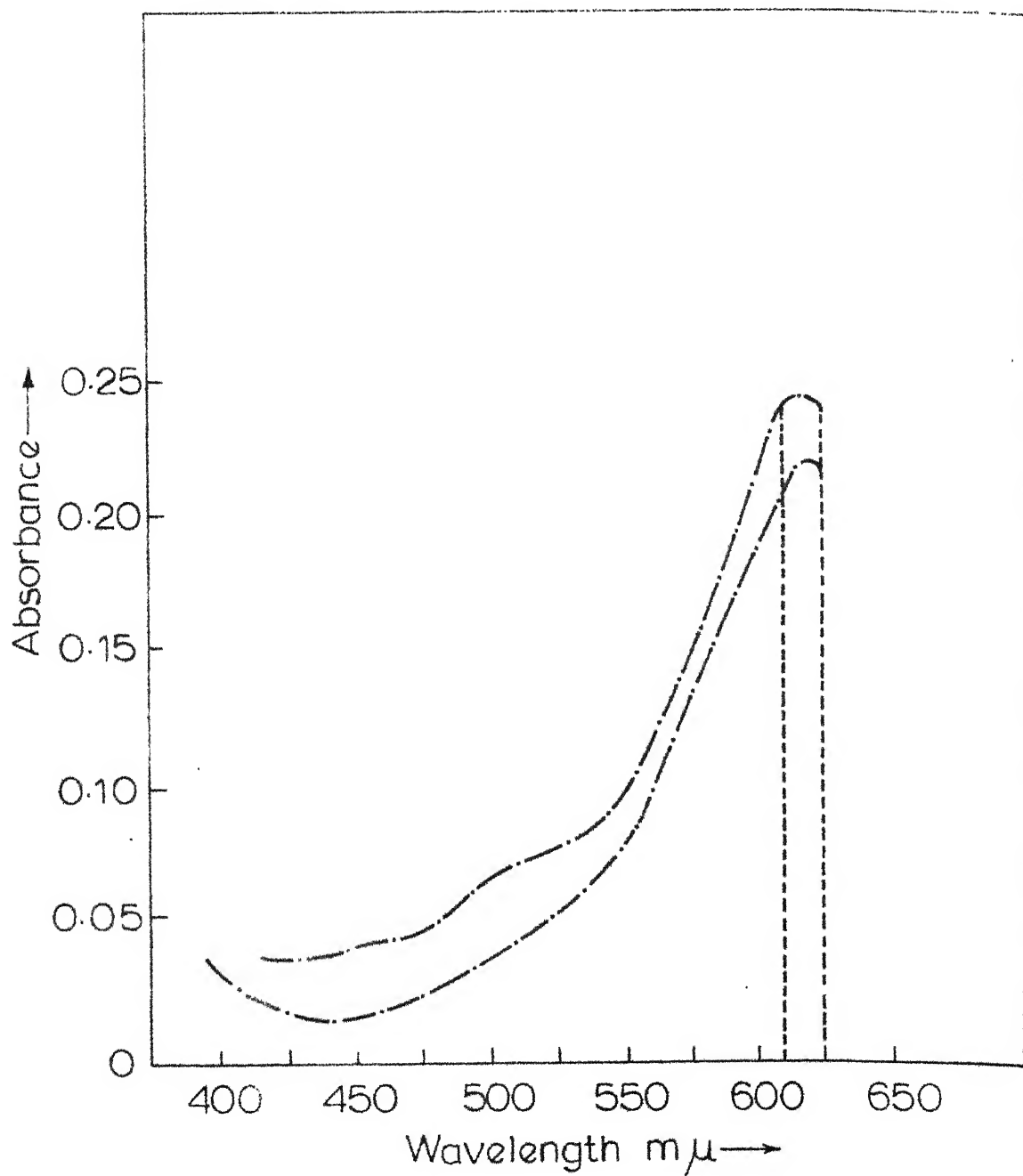
Fig.1

Estimation of Na-Oleate with Nile Blue Wavelength
Determination.
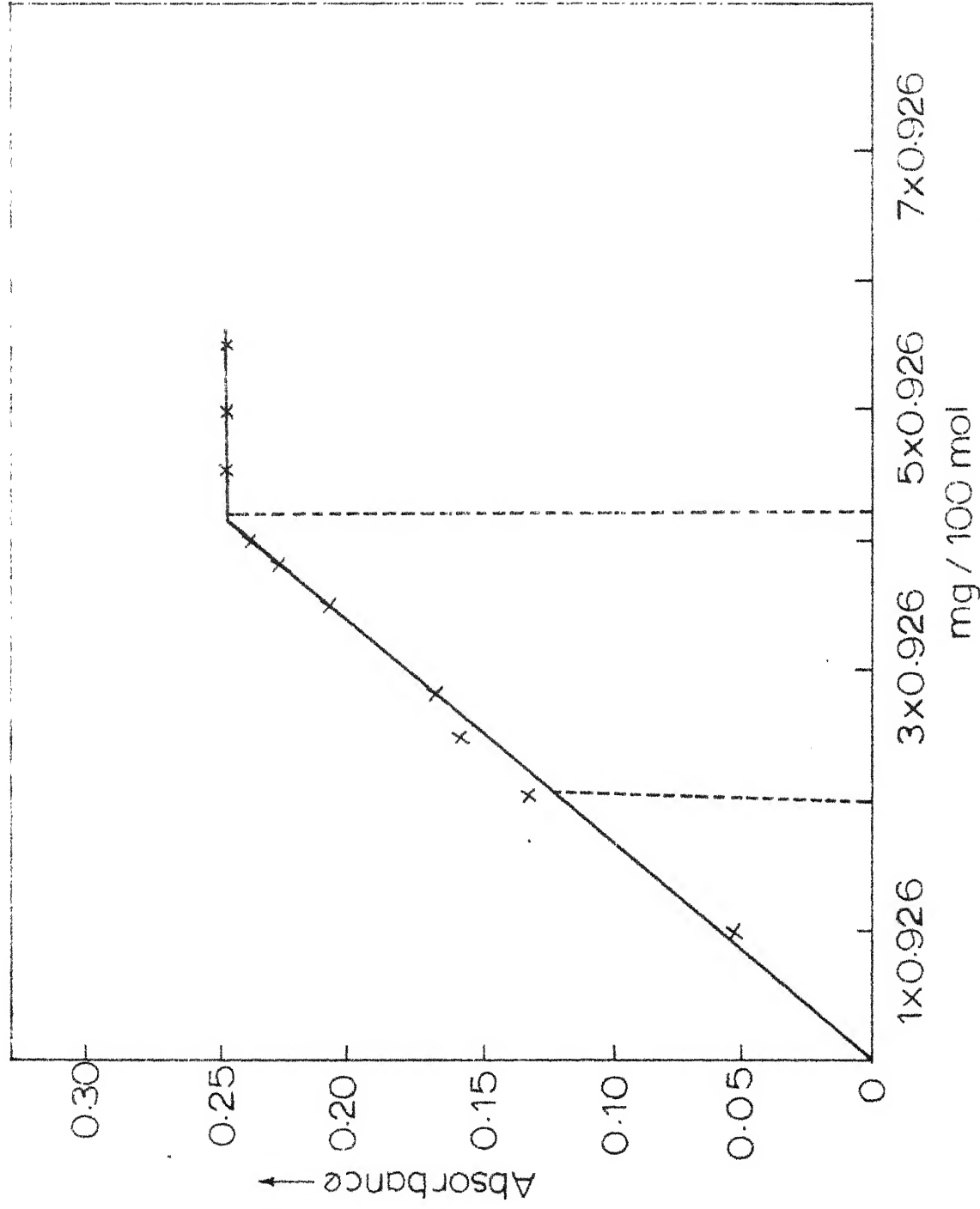
Estimation of Na-Oleate with Nile Blue Standard Curve

2.4 <u>MINERALS</u>: The minerals were supplied by the Indian Rare Earths Ltd., Quilon. Size analysis of the minerals was done with 500 gm sample. Table 2 shows the results of analysis. It is seen that most of the monazide lies within the narrow range of -60 to +140 mesh. Similarly zircon (Florida) lies in the range of -70 to +140 mesh and ilmenite in the range of -50 to +140 mesh. There are absolutely no fines in all mineral samples. Quantities finer than 140 mesh are negligible.

<u>TABLE 2</u>

<u>Size Analysis of the Minerals</u>

Sieve Size	Minerals		
Mesh	Monazite (Travancore)	Zircon (Florida)	Ilmenite (Travancore)
+ 45	0.00%	0.00%	0.10%
+ 50	0.49	0.00	8.73
+ 60	1.61	0.20	54.10
+ 70	65.90	0.33	31.20
+ 100	19.00	11.16	3.40
+ 120	8.45	50.00	1.11
+ 140	3.79	32.80	0.56
+ 170	0.00	0.74	0.00
+ 200	0.00	1.04	0.00
- 200	0.10	2.44	0.00
Losses	0.66	1.29	0.80
TOTAL :	100.00	100.00	100.00

<u>Chemical Assay</u>:- Chemical analysis of the minerals was done.

<u>Zircon</u>:- Weighed quantity was first heated strongly with

conc H_2SO_4 + $HClO_4$ mixture (2:1) for about 8 - 10 hours on a sand bath nearly to dryness and then sodium hydroxide fusion was performed at 230 °C. The fused mass was extracted with water. The solution was heated to boiling, pH adjusted between 1.5 - 2.5 and zirconium estimated colorimetrically with alizarin red-S which develops a red lake. Small amounts of Al, Fe etc. do not interfere.

Monazite:- The monazite sample contained no magnetics. It was treated with 1:1 hydrochloric acid to dissolve the surface impurities and then washed with distilled water. This was dissolved in concentrated sulphuric acid. The loss in weight gives the indication of the monazite content.

Ilmenite:- The sample supplied was of Q-grade and contained 58% TiO_2.

Table 3 summarises the chemical assay results. It is seen that the samples are fairly pure.

TABLE 3

Chemical Assay of Minerals

Minerals	Purity	Remarks
Monazite (Travancore)	97.00%	4% impurities (maximum)
Zircon (Florida)	95.9%	ZrO_2 64.4%
Ilmenite (Travancore)	96.7%	TiO_2 58%

CHAPTER - III

EXPERIMENTAL RESULTS

Correlation between adsorption and flotation properties of the minerals was sought. Two sets of experiments were performed: one set depicting the variation of flotation with pH and another the adsorption of sodium oleate with changes in pH.

3.1 FLOTATION EXPERIMENTS: In general, it is found that in case of anionic collectors the recovery changes with pH and shows a maximum at a certain pH and then falls. However, if sufficient collector is used the maxima is not well defined and the curve pH vs. percent recovery shows a flat plateau instead. This is evident in the results reported by K.K. Majumdar et. al(21) on monazite, ilmenite etc. In order, therefore, to get a well defined maximum comparatively lesser collector concentration is to be used. This has been done in case of the data presented in this section on monazite and ilmenite.

Experimental Procedure:- The mineral samples were weighed and transferred in glass containers and washed thoroughly in order to remove any surface contamination and soluble impurities. No acid washing was done in order to preserve the natural surface of the minerals.(It is a usual practice to give a mild acid wash in laboratory experiments; however, on industrial scale this is not done.) Denver sub A flotation cell was used for all the tests reported. A sketch of the cell is given in Figure 3. In essence, it has a suspended type mechanism, stainless steel shaft, impeller and diffuser, motor drive, variable speed control, adjustable

2'- 6"

3-1/2"

1000 GR.
500 GR.
250 GR

RUBBER PAD

1000 GRAM

500 GRAM

250 GRAM

OPTIONAL D-1 TANK SIZES
(STAINLESS STEEL TANKS)

Also available
in glass

RAISED
POSITION

ADJUSTABLE
SPEED CONTROL

SPEED INDICATOR
OPTIONAL

MECHANISM
RAISING CRANK
(SPRING
BALANCED)

LOCKING KNOB

STAINLESS
STEEL
MECHANISM

1/4 HP.
MOTOR

AIR CONTROL
VALVE
(EITHER SIDE)

PULP
AERATOR

3'-1-3/8"

2'-2-7/8"

2'- 2-1/4"

12"

LEVELLING SCREWS

HEAVY METAL BASE

FIG. 3
FLOTATION CELL

aeration control and tachometer. With the help of all these, one can very well regulate the air supply and speed of the stirrer. The glass cell used is of one litre capacity.

The mineral pulp was transferred to the cell and the collector solution in requisite quantities was added. This was followed by three minutes conditioning time after which little supernatent liquid was taken out for pH measurements. Dowfroth was added at this stage for frothing and flotation carried out for about 2.5 - 3 minutes. For each mineral data was obtained for two different collector concentrations in order to see whether the maximum is a function of concentration or not. Tables 4 and 5 give the data for ilmenite flotation with sodium oleate of strength 97.00 mg/l and 54.5 mg/l respectively. Tables 6 and 7 give flotation behaviour of monazite for oleate concentrations 38 mg/l and 80 mg/l respectively. In case of zircon all efforts to locate a well defined maximum were proved to be futile as it was flotable with small quantities (20 mg/l) of the collector over a wide pH range (see Appendix B). The data on ilmenite and monazite is plotted in Figures 4 and 5. A distinct maximum in case of both monazite and ilmenite is obtained.

TABLE 4

Variation of Ilmenite Recovery with pH

    Conditioning — 3 minutes at 600 R.P.M.
    Flotation   — 2 minutes at 1500 R.P.M.
    Frother   — 5 c.c. of 5% solution of Dowfroth-250
    Collector Concn- 96.7 mg/litre

S.No.	pH	Percent Recovery
1.	6.9	22.00
2.	7.1	30.00
3.	7.25	42.52
4.	8.32	92.50
5.	8.6	79.00
6.	9.15	69.80
7.	10.55	29.00

TABLE 5

Variation of Ilmenite Recovery with pH

Collector Concn : 54.5 mg/litre

S.No.	pH	Percent Recovery
1.	4.3	0.50
2.	6.80	18.50
3.	7.41	38.50
4.	8.05	55.05
5.	8.8	68.70
6.	9.46	34.50
7.	10.10	15.70
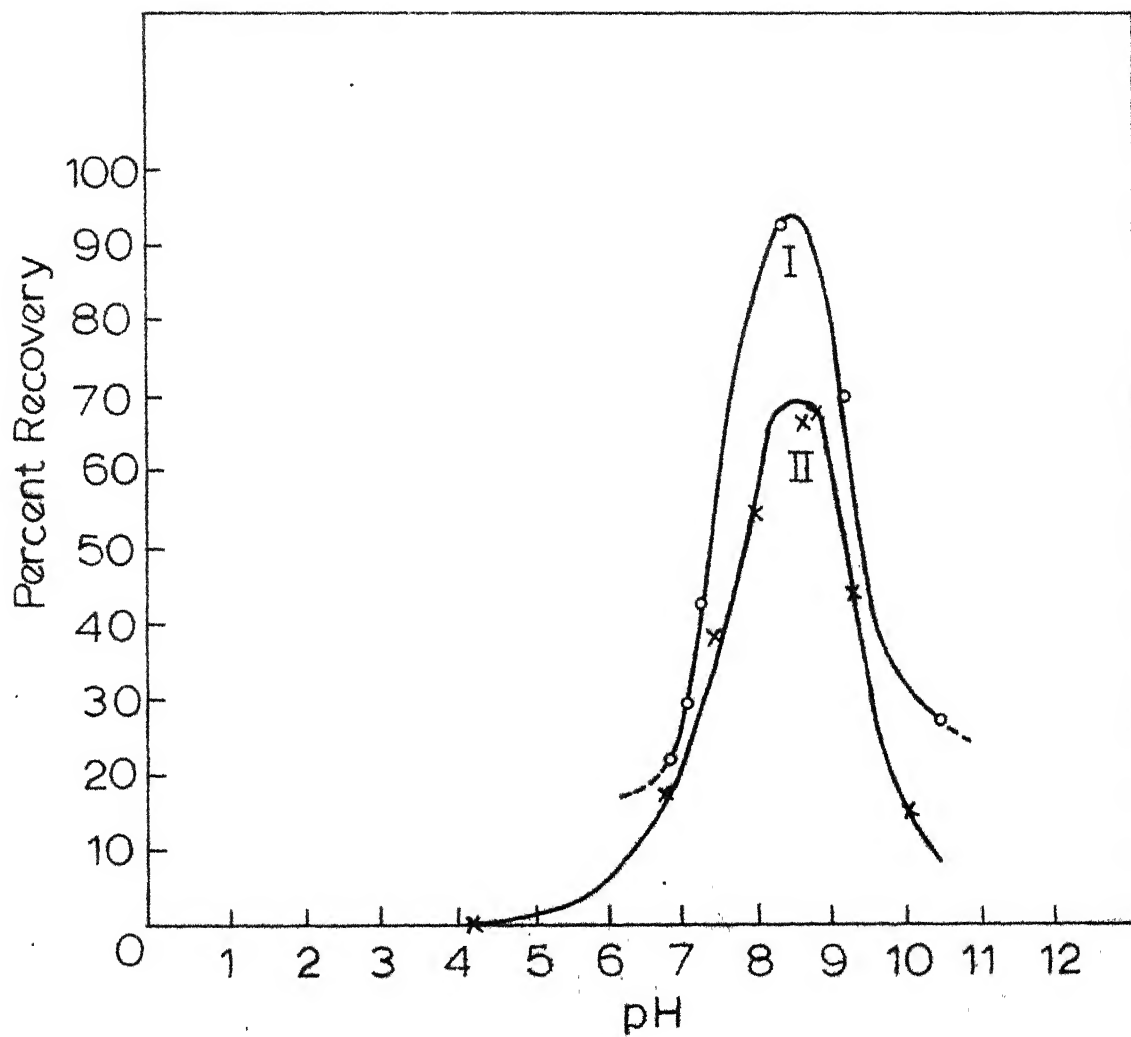
Fig. 4

Ilmenite-Na-Oleate
pH vs Percent Recovery
I - 96.7 mg/l
II - 54.5 mg/l

TABLE 6

Variation of Monazite Recovery with pH

   Conditioning - 3 minutes at 600 R.P.M.
   Flotation   - 2 minutes at 1400 R.P.M.
   Frother   - 5 c.c. of 5% solution of Dowfroth-250
   Collector Concn- 38.58 mg/litre

S.No.	pH	Percent Recovery
1.	5.45	1.00
2.	6.5	2.75
3.	7.2	24.20
4.	7.76	57.50
5.	8.23	60.00
6.	9.3	24.50
7.	9.82	22.50
8.	10.3	16.00

TABLE 7

Variation of Monazite Recovery with pH

Collector Concn - 79 mg/litre

S.No.	pH	Percent Recovery
1.	2.65	Nil
2.	5.73	3.00
3.	7.15	31.70
4.	7.25	54.70
5.	8.20	81.00
6.	8.80	67.50
7.	9.40	52.00
8.	10.00	34.50
9.	10.62	23.20
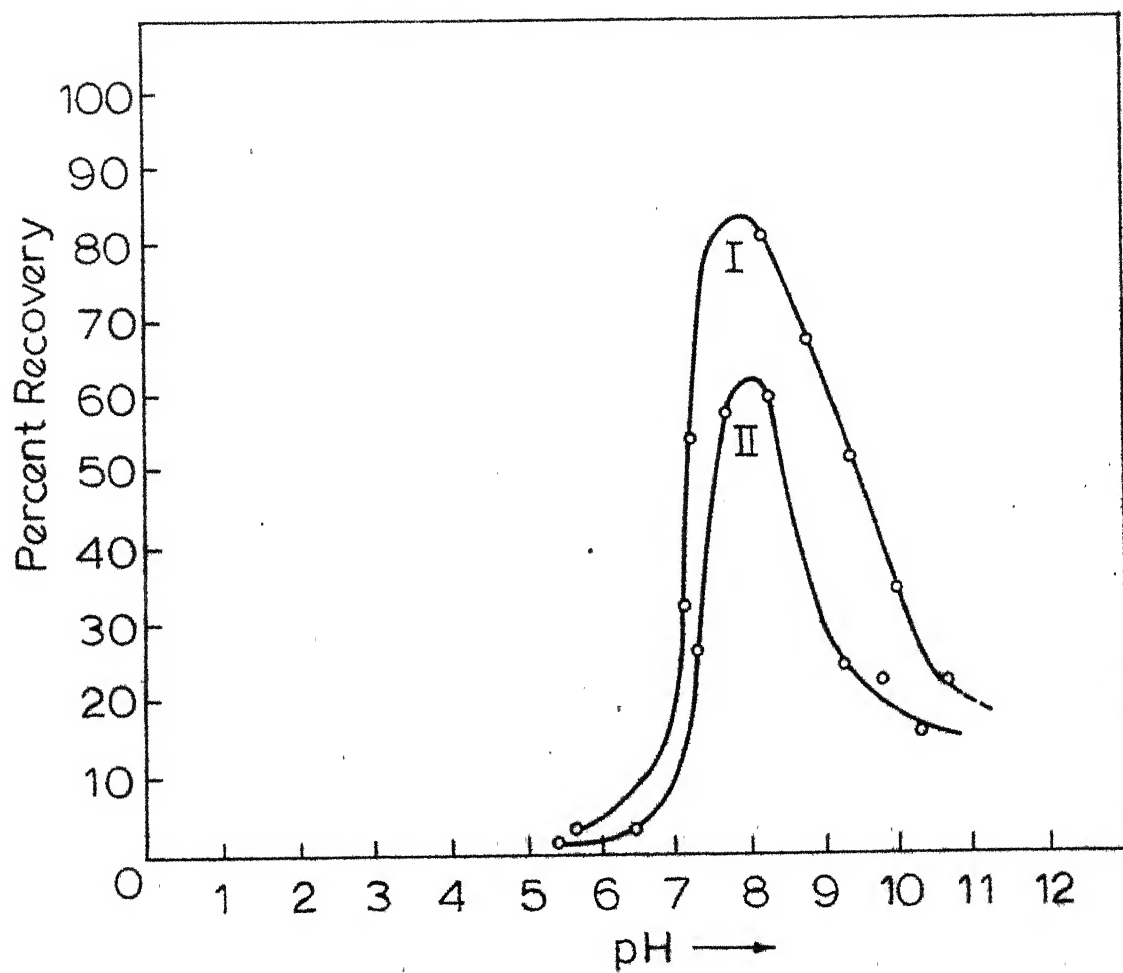
Fig. 5

Monazite -Na-Oleate
pH- Percent Recovery
I - 79mg/l
II - 38.6 mg/l

3.2 ADSORPTION EXPERIMENTS: The experiments were done under conditions similar to those in the flotation experiments. 10 gms of the mineral sample were taken in a beaker and washed thoroughly and repeatedly with distilled water and then transferred to stoppered reagent bottles. Any loss of weight during washing was estimated and necessary corrections made. To this, 125 ml of sodium oleate solution of appropriate concentration was added. The pH was varied by addition of sodium hydroxide or hydrochloric acid. The bottles were then shaken vigorously for about half an hour and then placed in a thermostat maintained at 35 $^\circ$C for about half an hour. After the contents of the bottle had reached the temperature of the bath the supernatent liquid was withdrawn and estimated for its oleate contents by colorimetric method described in Section 2.4. The initial and final or equilibrated pH of the solution was measured as also the electrode potentials. Beckmann research pH meter was used for the purpose.

Adsorption on the inner glass surface of the bottles was measured and necessary corrections made.

No effort was made to keep the total ionic concentration constant in order to keep the situation in the adsorption experiments similar to that present in the flotation experiments mentioned earlier.

Distilled water was used and hence CO_2 was not removed or avoided. Thus pH changes reported cannot be given any quantitative significance, although the trends are noteworthy.

Since the method of estimation is ineffective in the acidic region due to the excess Cl^- ions no measurements below pH 5.5 are reported.

The data on the adsorption of ilmenite, monazite and zircon is tabulated in Tables 8, 9 and 10 respectively. These are plotted in Figures 6, 7 and 8. It is found that in each case a maximum is obtained. Further discussion of the results is given in the Chapter IV along with flotation results.

TABLE 8

Effect of pH on the adsorption of Na-Oleate on Ilmenite

Initial Concentration of Na-Oleate - 3.32×10^{-4} mol/l

Temperature - $35\,^{\circ}C \pm 0.5\,^{\circ}C$

S.No.	Initial pH	Final pH	Initial Electrode Potential	Final Electrode Potential	Collector Adsorbed.
1.	3.834	6.390	+193.5 mV	+ 37.6 mV	8.14×10^{-7} mol/gms
2.	5.014	6.766	+122.3	+ 14.8	8.11×10^{-7}
3.	7.02	7.057	- 0.3	- 4.7	8.25×10^{-7}
4.	7.936	7.302	- 53.8	- 17.9	9.12×10^{-7}
5.	8.65	8.365	- 96.6	- 83.2	1.04×10^{-6}
6.	9.364	8.770	-138.1	-103.0	1.05×10^{-6}
7.	9.656	9.015	-157.9	-116.8	9.92×10^{-7}
8.	10.056	9.402	-179.2	-141.3	9.12×10^{-7}

TABLE 9

Effect of pH on the Adsorption of Na-Oleate on Monazite

Initial Concentration of Na-Oleate - 2.33×10^{-4} mol/litre

Temperature - $35\ ^{\circ}C \pm 0.5\ ^{\circ}C$

S.No.	Initial pH	Final pH	Initial Electrode Potential	Final Electrode Potential	Collector Adsorbed.
1.	5.016	6.530	+121.2 mV	+ 29.0 mV	6.25×10^{-7} mol/gm
2.	7.166	7.204	- 4.0	- 12.4	6.67×10^{-7}
3.	8.14	7.774	- 66.2	- 46.3	7.32×10^{-7}
4.	7.99	7.840	- 54.0	- 52.0	8.20×10^{-7}
5.	8.58	8.424	- 93.2	- 84.2	9.82×10^{-7}
6.	8.876	8.450	-	-	9.82×10^{-7}
7.	9.376	8.786	-	-	8.20×10^{-7}
8.	9.966	9.760	-147.2	-147.2	7.34×10^{-7}
9.	10.290	10.204	-	-	7.34×10^{-7}

TABLE 10

Effect of pH on the Adsorption of Na-Oleate on Zircon

Initial Concentration of Na-Cleate - 2.33 x 10^{-4} mol/litre

Temperature - 35 $^{\circ}$C $\pm$ 0.5 $^{\circ}$C

S.No.	Initial pH	Final pH	Initial Electrode Potential	Final Electrode Potential	Collector Adsorbed.
1.	4.66	5.380	+141.7 mV	+ 96.0 mV	9.09 x 10^{-7} mol/gm
2.	6.00	6.434	+ 57.2	+ 34.0	9.09 x 10^{-7}
3.	6.374	6.974	-	-	9.82 x 10^{-7}
4.	7.132	7.124	- 9.4	- 8.0	9.52 x 10^{-7}
5.	8.070	7.270	- 64.2	- 14.8	9.99 x 10^{-7}
6.	8.246	7.350	- 74.4	- 22.4	1.08 x 10^{-6}
7.	8.410	8.000	- 84.6	- 62.4	1.39 x 10^{-6}
8.	8.610	8.126	- 96.6	- 67.2	1.13 x 10^{-6}
9.	8.628	8.474	- 96.2	- 88.0	1.17 x 10^{-6}
10.	9.272	9.308	-124.1	-130.4	8.20 x 10^{-7}
11.	10.326	9.910	-189.4	-166.2	6.67 x 10^{-7}
12.	10.834	10.562	-221.3	-206.0	4.80 x 10^{-7}
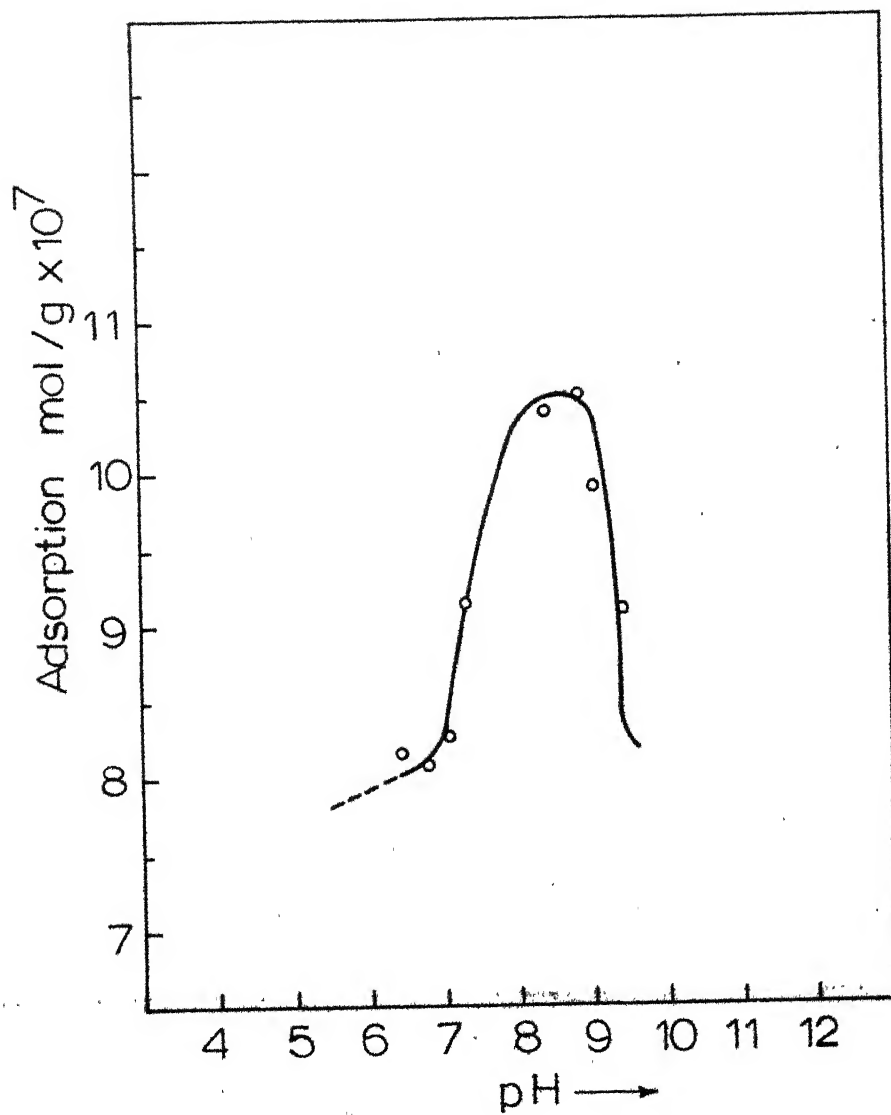
Fig. 6

Ilmenite - Na - Oleate

Variation of Adsorption with pH.
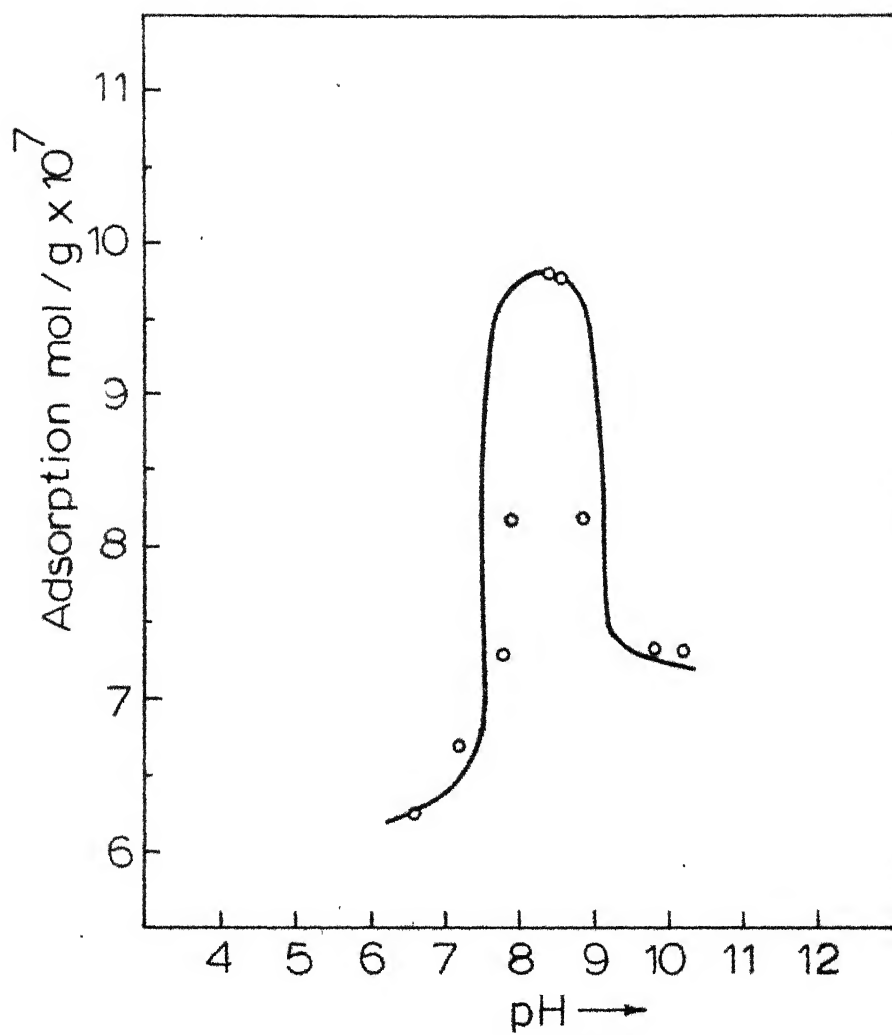
Fig. 7

Monazite - Na - Oleate
Variation of Adsorption with pH.
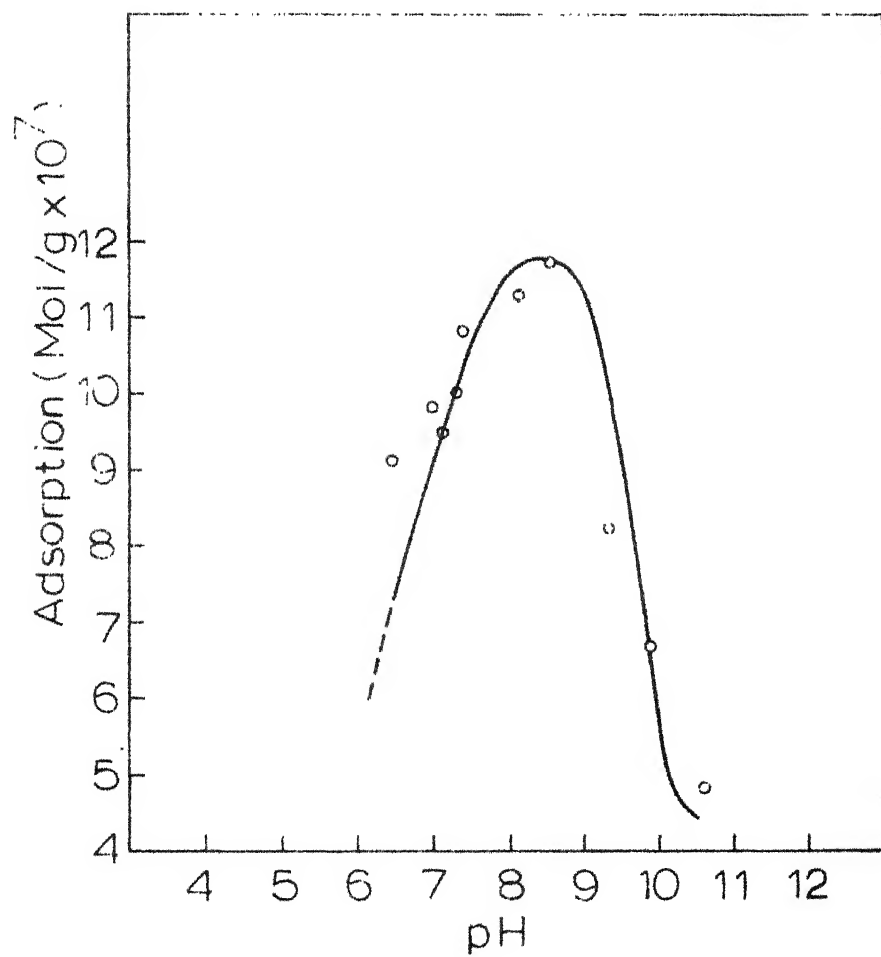
Fig. 8

Zircon - Na - Oleate
Variation of Adsorption with pH.

CHAPTER - IV

DISCUSSION OF RESULTS

4.1 EXPERIMENTAL BEHAVIOUR:

Flotation Curves:- In general, the flotation curves obtained are bell-shaped. With increasing pH, the per cent recovery increases, attains the maximum and then falls.

In case of ilmenite the maximum occurs at pH 8.5. It is seen from Figure 4 that for two concentrations of the collector the maximum is not shifted appreciably.

In case of monazite the maximum recovery is obtained between pH 8.1 - 8.3. Here also the maxima is hardly shifted when the collector concentration is changed from 38 mg/l to 79 mg/l. This is evident from Figure 5.

Flotation with zircon gave a wide plateau and maximum could not be located even after using concentrations as low as 25 mg/l (see Appendix B).

Adsorption Curves:- In general, the adsorption curves presented the general features of the flotation curves indicating thereby that adsorption of sodium oleate and flotation are closely related.

In case of ilmenite, the maximum on the adsorption curve falls at pH 8.5 - 8.7 while in case of monazite and zircon it occurred at pH 8.1 - 8.3 and 8.3 - 8.5 respectively (Figures 6, 7 and 8).

Flotability of the Minerals:- Though a direct relative flotation behaviour of the three minerals cannot be judged from these adsorption curves since the minerals differ markedly in

their size distribution and location, it may be stated that more adsorption results in more flotation. Hence the order in which the flotability of the above three minerals can be arranged, depending on their adsorption magnitudes, is zircon > monazite > ilmenite. According to Taggart(33) the descending order of flotability is zircon, monazite and ilmenite which is the same as obtained on the basis of the present work. However, from the work of K.K. Majumdar et.al (21,22) the order should be monazite > zircon > ilmenite. This has a support from Nutt's(34) hypothesis which states that in case of silicate and oxide minerals the greater the complexity of the structure of the minerals the greater will be the possibility of collector attacking centres. Thus monazite which is a complex phosphate (Ce, Dy, Nd)PO_4 should be more amenable to attack by collector ions than zircon which is less complex, it being a simple silicate ($ZrSiO_4$). On the other hand, the results obtained by R. Mallikarjunan et.al(20) suggest greater flotation activity for zircon than for monazite when sodium linoleate and sodium linolenate are used as collectors. The conflicting situation can be resolved only if the adsorption density values on the mineral surfaces are measured.

4.2 EXPERIMENTAL CORRELATION BETWEEN ADSORPTION AND FLOTATION:

As has been mentioned earlier, the adsorption and flotation experiments were done under almost identical conditions. However, there is one basic difference in the two sets. Whereas the interface involved in flotation is air-solid-water interface, the one in adsorption is solid-water interface. D.W. Fuerstenau(25) showed in case of quartz-dodecylamine acetate system that there is

experimental correlation between adsorption and flotation. In
Figures 9 and 10 are shown the adsorption and flotation curves
superimposed in case of ilmenite and monazite respectively. It
is found that the adsorption and flotation maximum coincide
excellently in both the cases. Secondly adsorption curves follow
the flotation curves, showing that there is an overall experimental
correlation between adsorption and flotation.

4.3 pH, ADSORPTION AND FLOTATION: Explanation for the general
shape of the adsorption and flotation curves is to be sought in
the prevailing ionic conditions in the aqueous bulk phase and the
effects of different ionic species, e.g., H^+ , OH^- , etc. on
adsorption.

Qualitatively, the action of H^+ and OH^- ions on the
collector adsorption can be divided into following:

1) The concentration of hydrogen ions affect the degree of
   dissociation of collector into ions.

2) H^+ and OH^- ions get adsorbed either in the internal
   or external part of the double layer changing the
   electrochemical and electrokinetic potential and thus
   affect the collector adsorption on to the surface or
   in the double layer.

3) Hydroxyl ions can compete with collector anions and
   hydrogen ions with cations during their adsorption on the
   surface.

4) They can remove or favour adsorption of other ions which
   are detrimental to the adsorption of the collector.
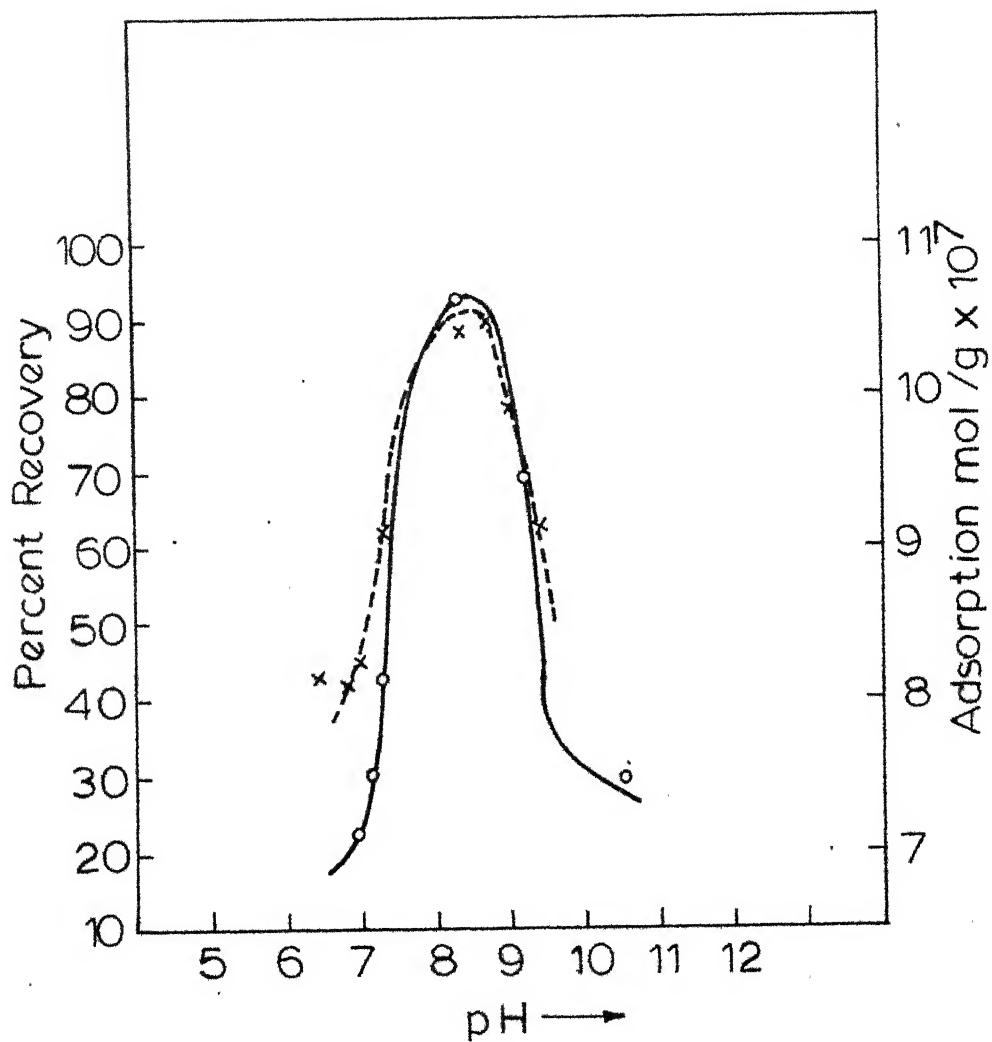
Fig. 9

Ilmenite -Na Oleate

Flotation Curve ——o——
Adsorption Curve ----x----
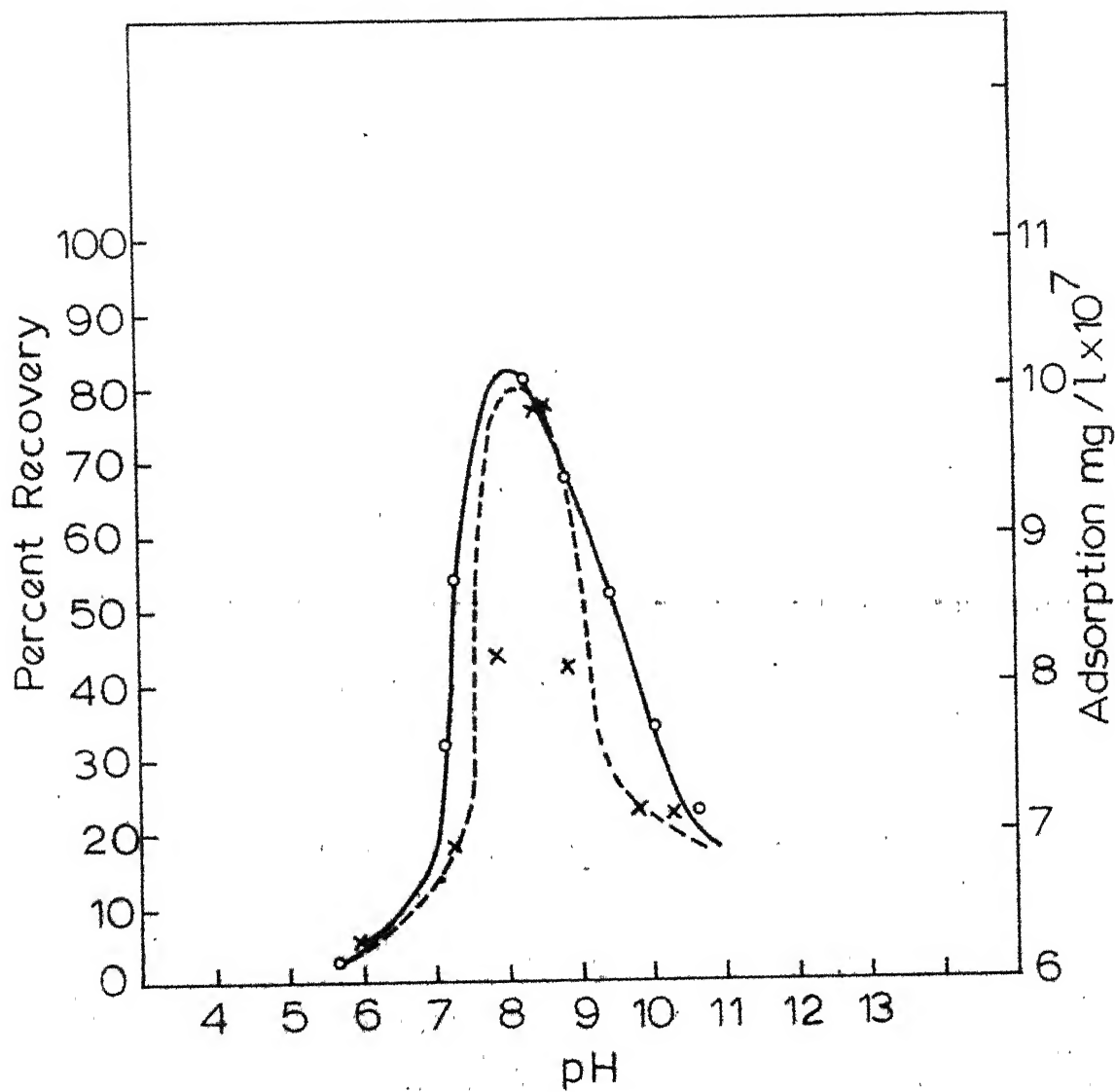
Fig. 10

Monazite - Na - Oleate

Flotation Curve——○——

Adsorption Curve----○----

The first of these is more important in case of flotation with fatty acid soaps such as sodium oleate.

Oleate Ion Concentrations at different pH Values:- In these systems, the following ionic equilibria exist in the aqueous bulk phase.

$$Ol_s^- + Na^+ + H_2O \underset{I}{\overset{K_h}{\rightleftharpoons}} HOl_s + Na^+ + OH^-$$

$$III \quad\quad II \Big\Vert \quad K_F \quad\quad\quad (a)$$

$$K_d$$

$$(Ol_m^- , HOl_m)$$

$$H^+ + OH^- \rightleftharpoons H_2O \quad\quad\quad\quad (b)$$

$$H^+ + Cl^- \rightleftharpoons HCl \quad\quad\quad\quad (c)$$

$$Na^+ + OH^- \rightleftharpoons NaOH \quad\quad\quad\quad (d)$$

$$HOl_s \rightleftharpoons H^+ + Ol_s^- \quad\quad\quad\quad (e)$$
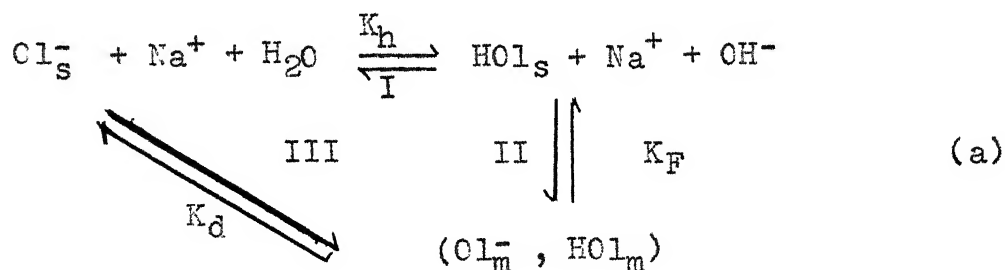
where Ol^- represents oleate ions and m stands for micelle and s for solution phase. Two distinct cases have to be realised:

1) for concentrations below critical micelle concentration (c.m.c.), and

2) above the critical micelle concentfations.

For Concentrations below c.m.c. :- Of the above reactions (c) and (d) involve strong electrolytes and are instantaneous reactions; (e) is negligible since HOl is sparingly soluble in water. Also as far as reaction (a) is considered, steps II and III do not come into picture below c.m.c. Thus, for the hydrolysis reaction (a), we have

$$\frac{c_{HOl} \cdot c_{OH^-}}{c_{Ol^-}} = K_h \quad\quad\quad \ldots \quad (4.1)$$

where C's represent concentrations and K_h is the hydrolysis constant. From a mass balance on oleate ions we have

$$S = C_{Ol^-} + C_{HOl} \qquad \qquad \cdots \quad (4.2)$$

where S is actual concentration of sodium oleate solution added in mol/litre.

Hence from (4.1) and (4.2), we get

$$C_{Ol^-} = \frac{S \cdot C_{OH^-}}{(K_h + C_{OH^-})} \qquad \qquad \cdots \quad (4.3)$$

now, below c.m.c., i.e., when $S \ll$ c.m.c. and in the absence of excess alkali, the degree of hydrolysis β which is the fraction of a gm mol. of sodium oleate hydrolysed at equilibrium is related to K_h by

$$K_h = \frac{\beta^2 \ S}{1-\beta} \qquad \qquad \cdots \quad (4.4)$$

Also

$$C_{H^+} \cdot C_{OH^-} = 10^{-14} \qquad \qquad \cdots \quad (4.5)$$

Hence equation (4.3) reduces to

$$C_{Ol^-} = \frac{S \cdot 10^{(pH - 14)}}{\dfrac{\beta^2 \ S}{1-\beta} + 10^{(pH-14)}} \qquad \qquad \cdots \quad (4.6)$$

Thus if the value of K_h is known C_{Ol^-} can be calculated for any value of $S \ll$ c.m.c. at different pH values.

It is to be noted at this place that β is not strictly independent of pH. As a matter of fact, it changes and the equation (4.4) does not hold good except for the natural pH values in which case measured β values are available in the literature(34a). However, irrespective of any changes in β the value of K_h at any temperature remains substantially constant.

Hence the value of K_h calculated on the basis of β values at the natural pH can be used without any loss of accuracy and generality.

The values of β for different concentrations at natural pH as also the calculated values of $C_{Ol_S^-}$ are given in Appendix C. These values are plotted in figure 11 for $S = 3.32 \times 10^{-4}$ mol/litre.

For the case when S exceeds c.m.c. we have to take into consideration the steps II and III in reaction (a). In the present work the range of concentrations used is much less than c.m.c. which is around 1.5×10^{-3} mol/litre for sodium oleate; hence, we need not consider this case. However, the expression for calculating the C_{Ol^-} in this case has also been derived and is reported in Appendix D.

4.4 <u>ADSORPTION AND OLEATE ION CONCENTRATION</u>: It is seen from the figure 11 that as the pH increases the C_{Ol^-} values also increase; and after pH 9 or 10, remain constant.

If we postulate that the collector sodium oleate gets adsorbed on to the mineral surface in the form of oleate ion species then the adsorption should increase continuously with pH and attain some constant values in higher pH range, and we may expect the adsorption density to be proportional to some power of C_{Ol^-} , or

$$\Gamma = K_1 \, C_{Ol^-}^{n_1} \qquad \qquad \ldots \ (4.7$$

where Γ is adsorption per gram of the mineral and K_1 and n_1 are empirical constants.
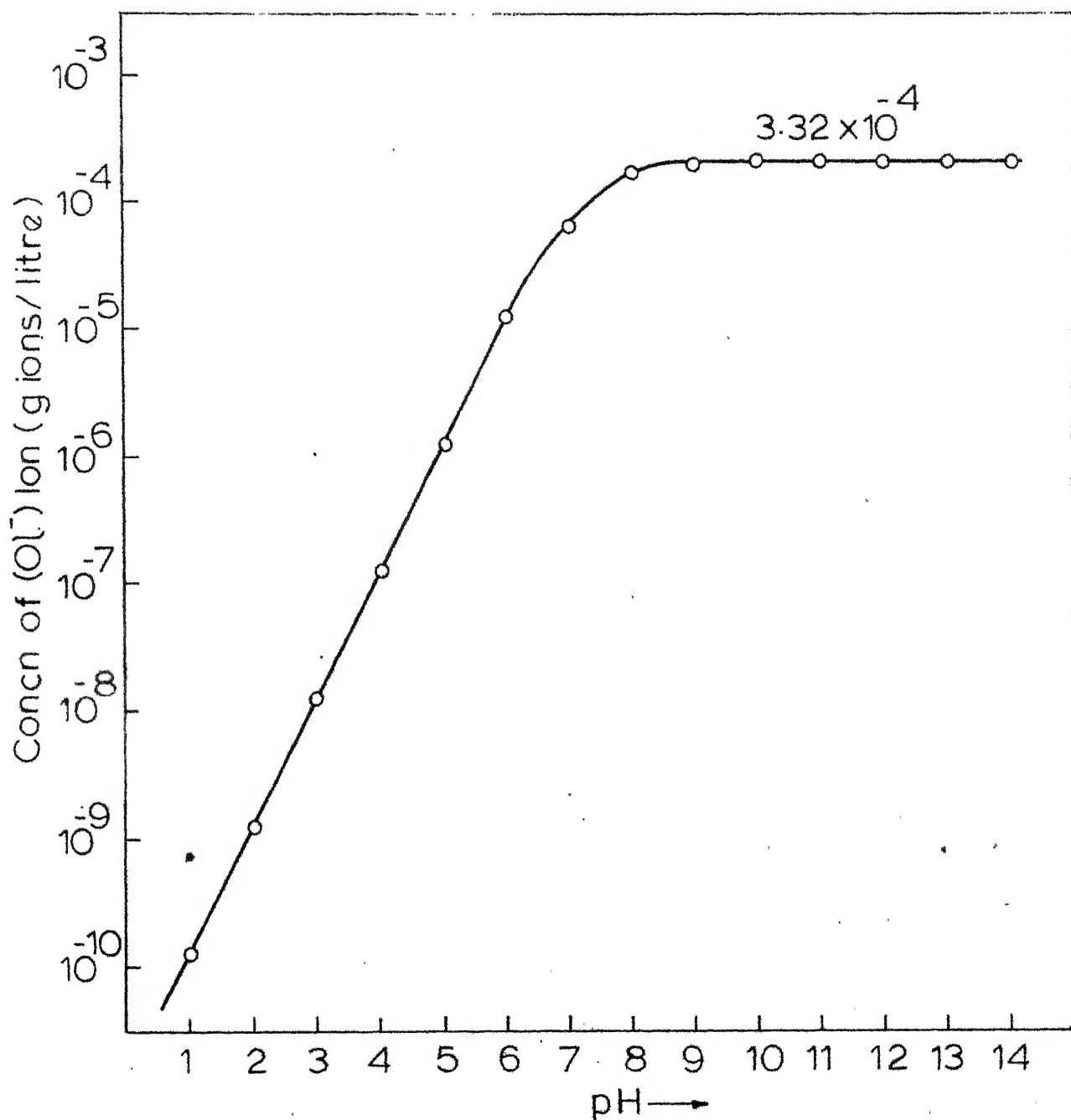
Fig. 11

Variation of Oleate Ion Concentration with pH.

If the above contention is true then,

$$\log \Gamma = \log K_1 + n_1 \log C_{01^-} \qquad \ldots \quad (4.8)$$

and a plot of $\log \Gamma$ versus $\log C_{01^-}$ should be a straight line with slope n_1. In Figure 12, the data in the acidic range for ilmenite, monazite and zircon is plotted to test the aforesaid. The excellent straight line plots obtained in case of all the three minerals, prove that the contention is true in the acidic range. The values of K_1 and n_1 can be found out from these plots. However, as can be seen from the Figures 14, 15 and 16, the adsorption magnitude instead of remaining constant as indicated by eqn. (4.7), falls crisply in the alkaline region. The dotted lines in the above figures indicate the adsorption value expected according to equation (4.7) for the entire pH range. Satisfactory fit in the acidic range is evident.

However, the situation predicted by the equation (4.7) is not experimentally realised at higher pH values. Some additional factor is obviously playing an important role.

It need not be restressed that OH^- ion acts as a competitor to the collector anion for getting adsorbed on suitable sites. Adsorption is, therefore, also dependent on the ratio $\dfrac{C_{OH^-}}{C_{01^-}}$ and a general equation of the type

$$\Gamma = K_1 \, C_{01^-}^{n_1} - K_2' \left[\frac{C_{OH^-}^{n_2}}{C_{01^-}} \right]^m \qquad \ldots \quad (4.9)$$

can be postulated.

From previous discussion (see Figure 11) the C_{01^-} in the alkaline region almost remains constant. Also as a first approximation taking $m = 1$ we have

Plot of log (ol⁻)ₛ against log Γ
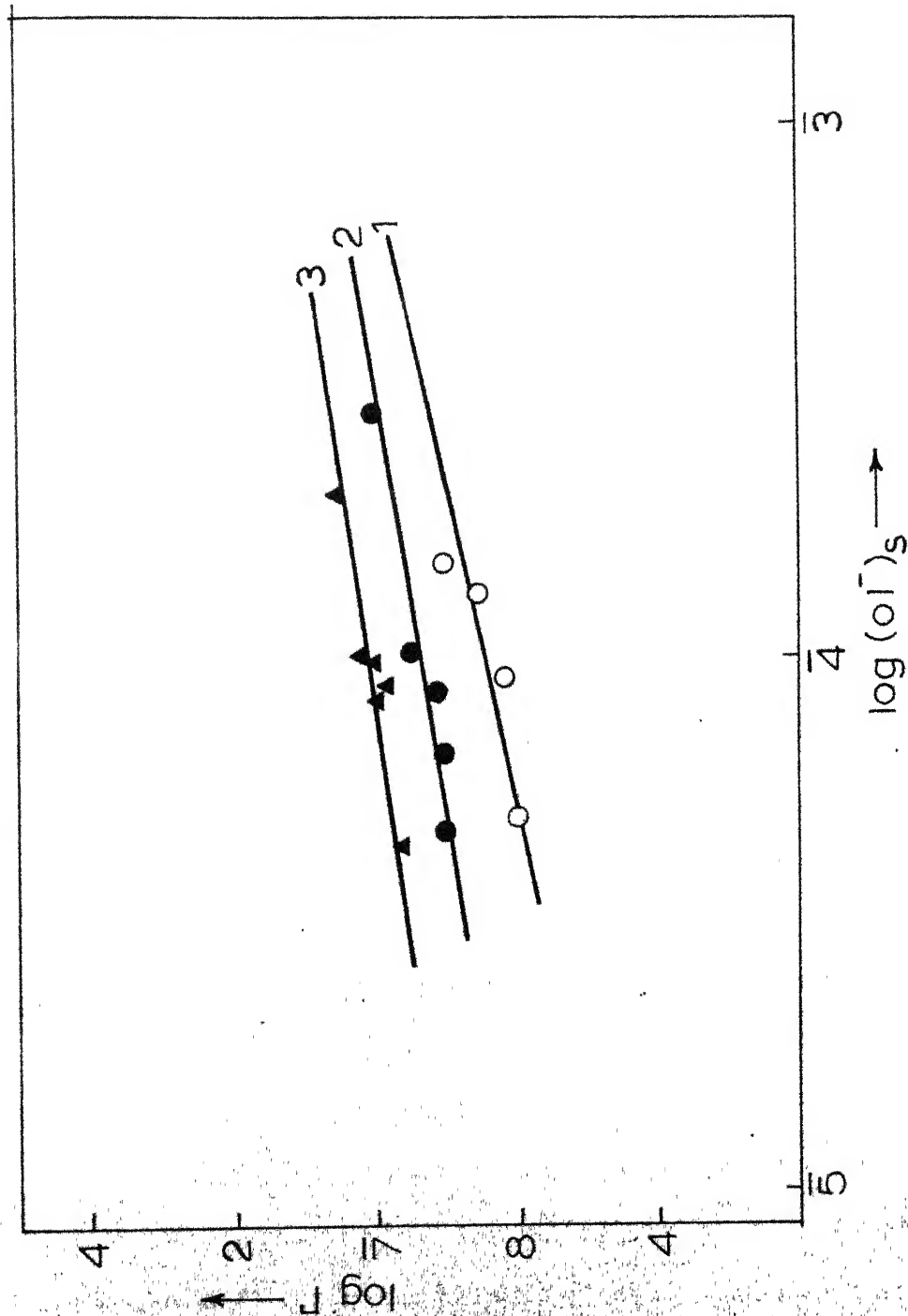
Fig. 12

1. Monizile
2. Ilminite
3. Zircon

$$\Gamma = \Gamma' - K_2' \, c_{OH^-}^{n_2} \qquad\qquad \ldots \quad (4.10)$$

where $\Gamma' = K_1 \, c_{Ol^-}^{n_1}$ (= constant for high pH values)

and $K_2 = \dfrac{K_2'}{c_{Ol^-}} = $ constant

Hence $\log(\Gamma' - \Gamma)$ when plotted against $\log c_{OH^-}$ should give a straight line for the alkaline region from which K_2 and m are found out. In Figure 13 the data for all the three minerals is plotted. It is seen therefrom that except for ilmenite the straight line relationship is not strictly obeyed.

It would be interesting to see how far eqn. (4.10) fits in with the experimental data. In Figures 14, 15 and 16 the continuous lines with open circles show the theoretically calculated values of Γ on the basis of eqn. (4.10). It is seen that in acidic as well as alkaline region the theoretical curve adequately fits the experimental data. In the vicinity of the maximum, on the other hand the fit is poor and the theoretical values are somewhat lower than the experimental ones. The deviation is less in case of ilmenite and somewhat more pronounced in case of monazite and zircon.

The discrepancy may be attributed to the following reasons:
1) comparatively large error in the experimental determinations of the adsorption magnitude.

This is probable because in the region of the maximum the concentration of sodium oleate in the supernatent liquid
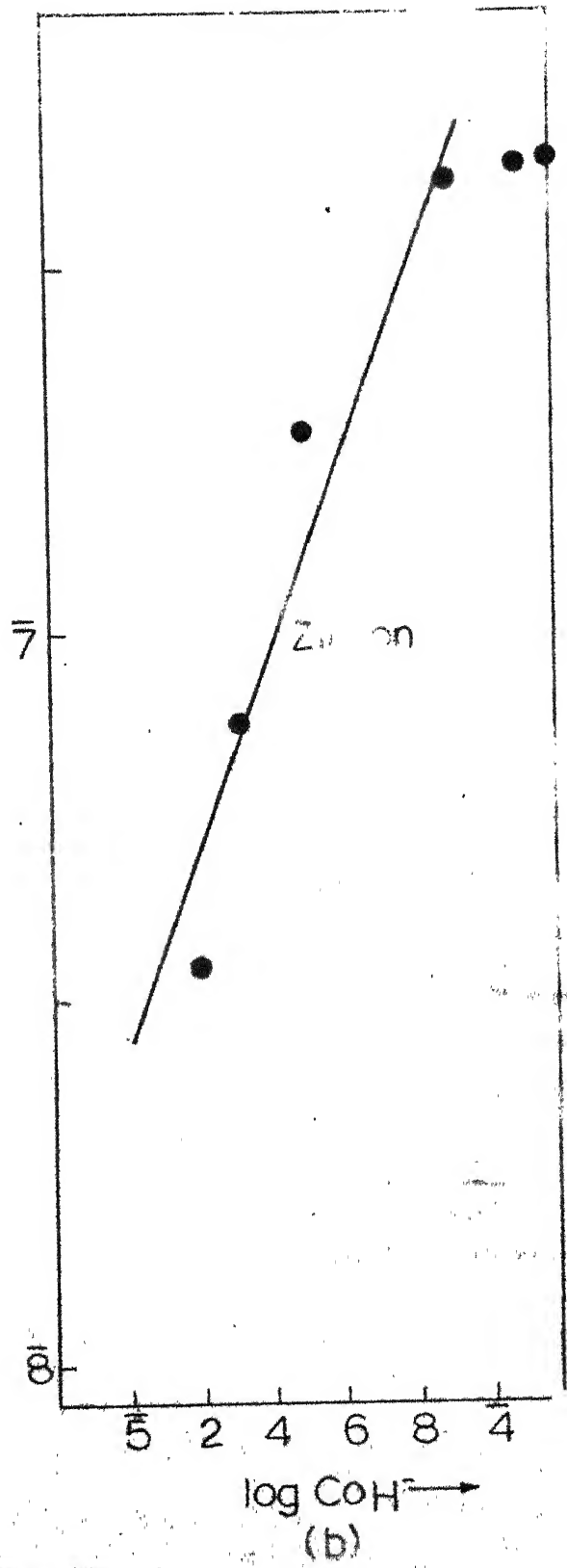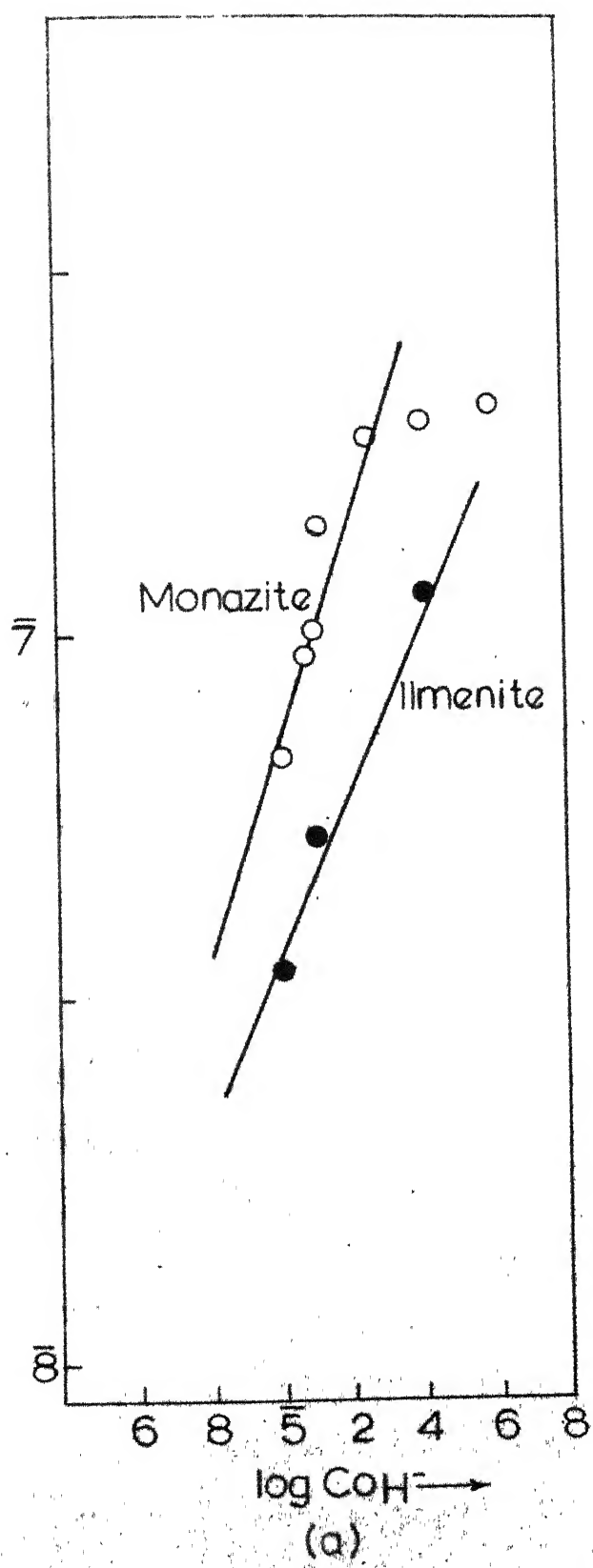
Fig.13

Plot of log $(\Gamma' - \Gamma)$ vs. log C_{OH^-}

2) Inherent inadequacy of the eqn. (4.10). This is evident from the deviations exhibited from the straight line relationship in Figure 13.

Better fit may be obtained by assuming a more sophisticated expression in place of the second term in eqn. (4.10), e.g., expressions including higher order terms. However, this idea is not pursued further, since eqn. (4.10) is reasonably adequate.

Furthermore, the maxima obtained by eqn. (4.10) tally well with the experimental ones as is evident from the following:

	Adsorption Maximum	Flotation Maximum	Theoretical Adsorption Maximum
Ilmenite	8.5. - 8.7	8.5 - 8.7	8.6 - 8.7
Monazite	8.1 - 8.3	8.1 - 8.3	8.1 - 8.3
Zircon	8.3 - 8.5	. -	8.4

In addition to the general shape and fairly good fit in the acidic and alkaline region as well as predicting proper magnitude of the maximum, eqn. (4.10) can also successfully explain the occurrence of a flat plateau when higher concentrations are used. In such cases the first term is more predominant and the OH^- ion effect is felt at a higher pH value. Thus a flat portion as given by the first term appears in adsorption and flotation curves before the value finally drops down markedly.

Thus it is concluded that there exists a distinct correlation between flotation and adsorption magnitude.

The general behaviour is dependent on the C_{O1^-} and C_{OH^-} / C_{O1^-} and a quantitative relationship such as eqn. (4.10) can be obtained.
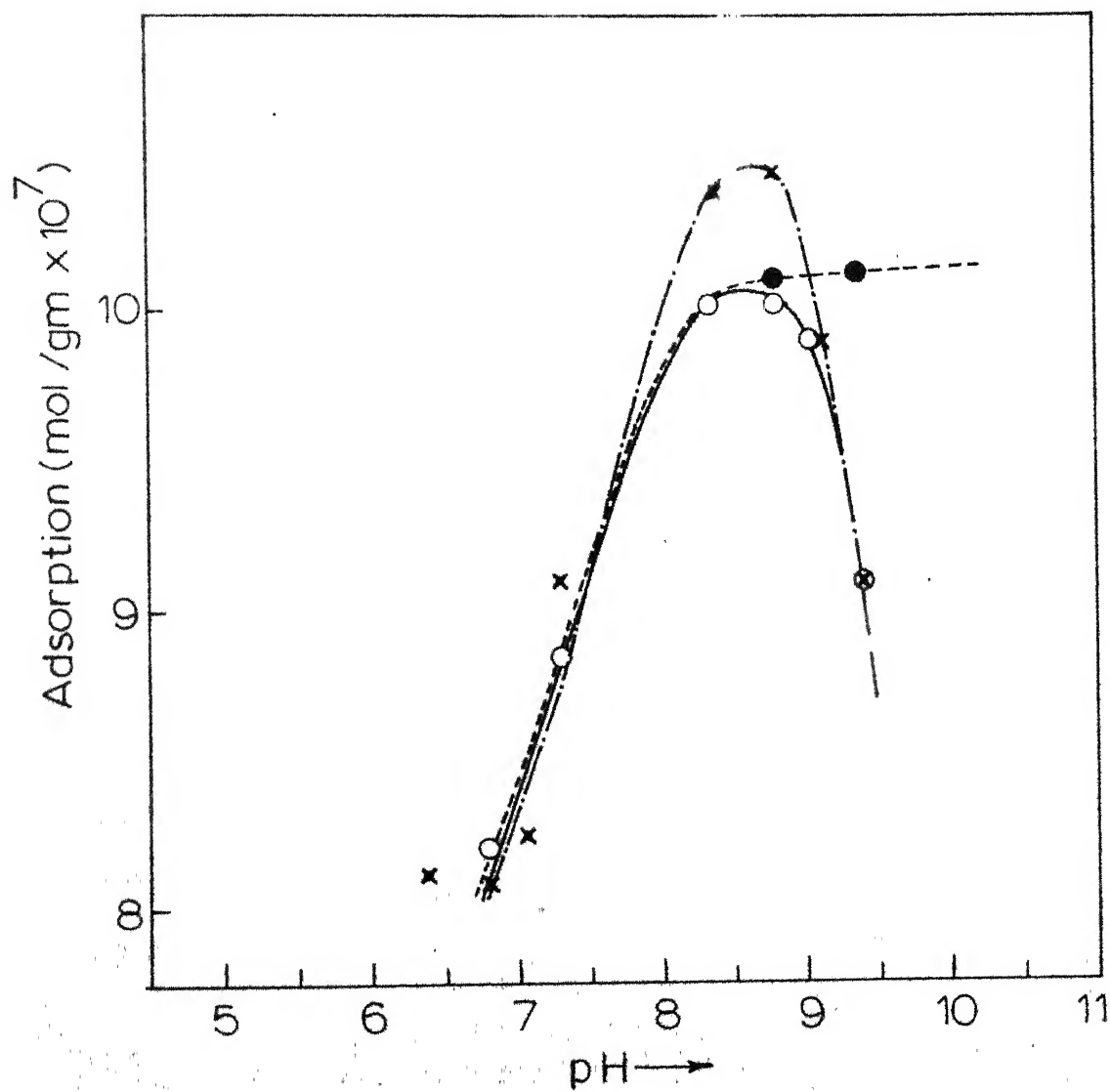
Fig.14

Ilmenite-Na-Oleate

Variation of Adsorption with pH.

Experimental ————x———

Theoretical (4·10)————o————

Theoretical (4·7)————•————
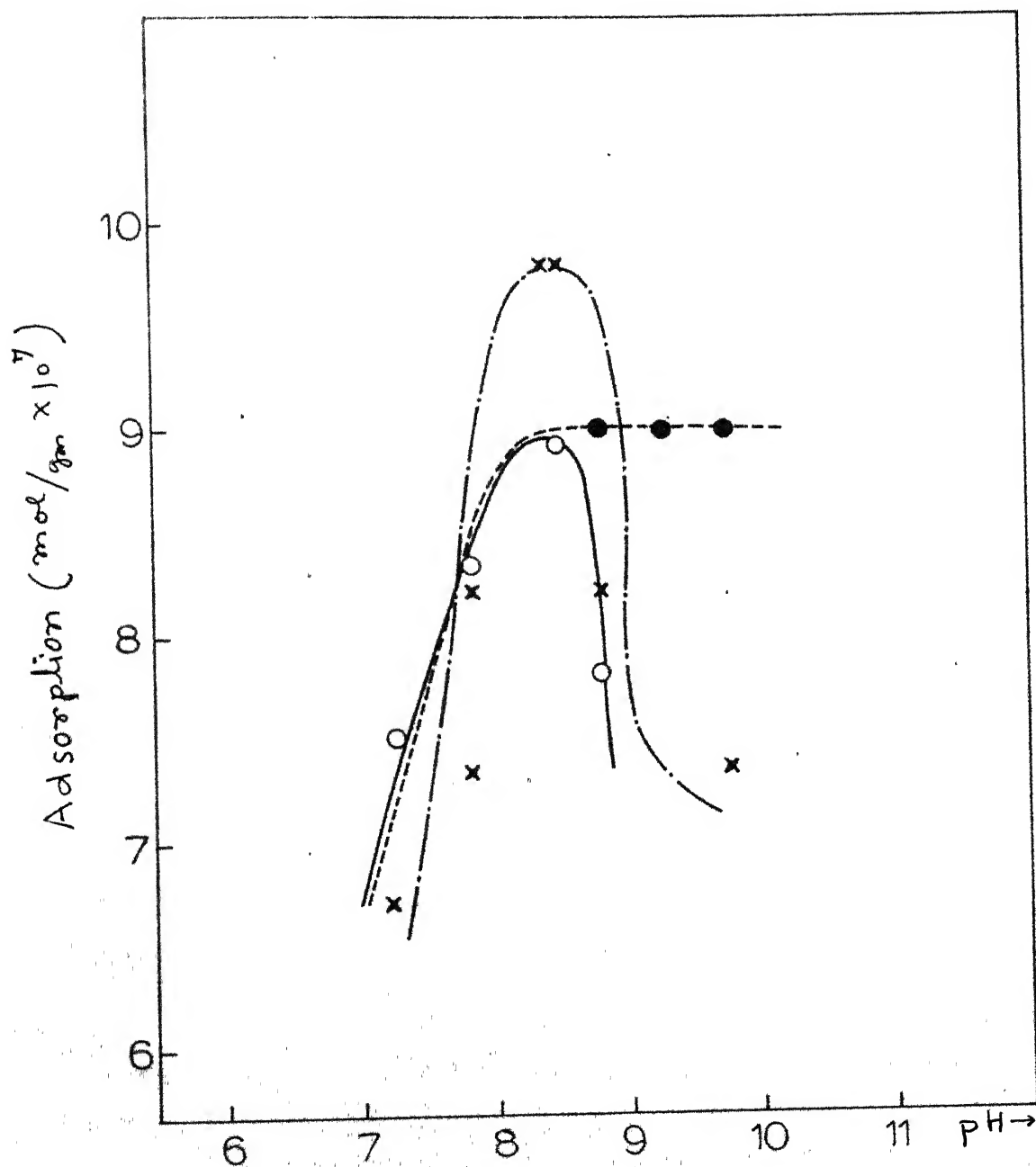
Fig. 15

Monazite-Na-Oleate

Variation of Adsorption with pH.

Experimental ——×——

Theoretical (4.7) ----●----
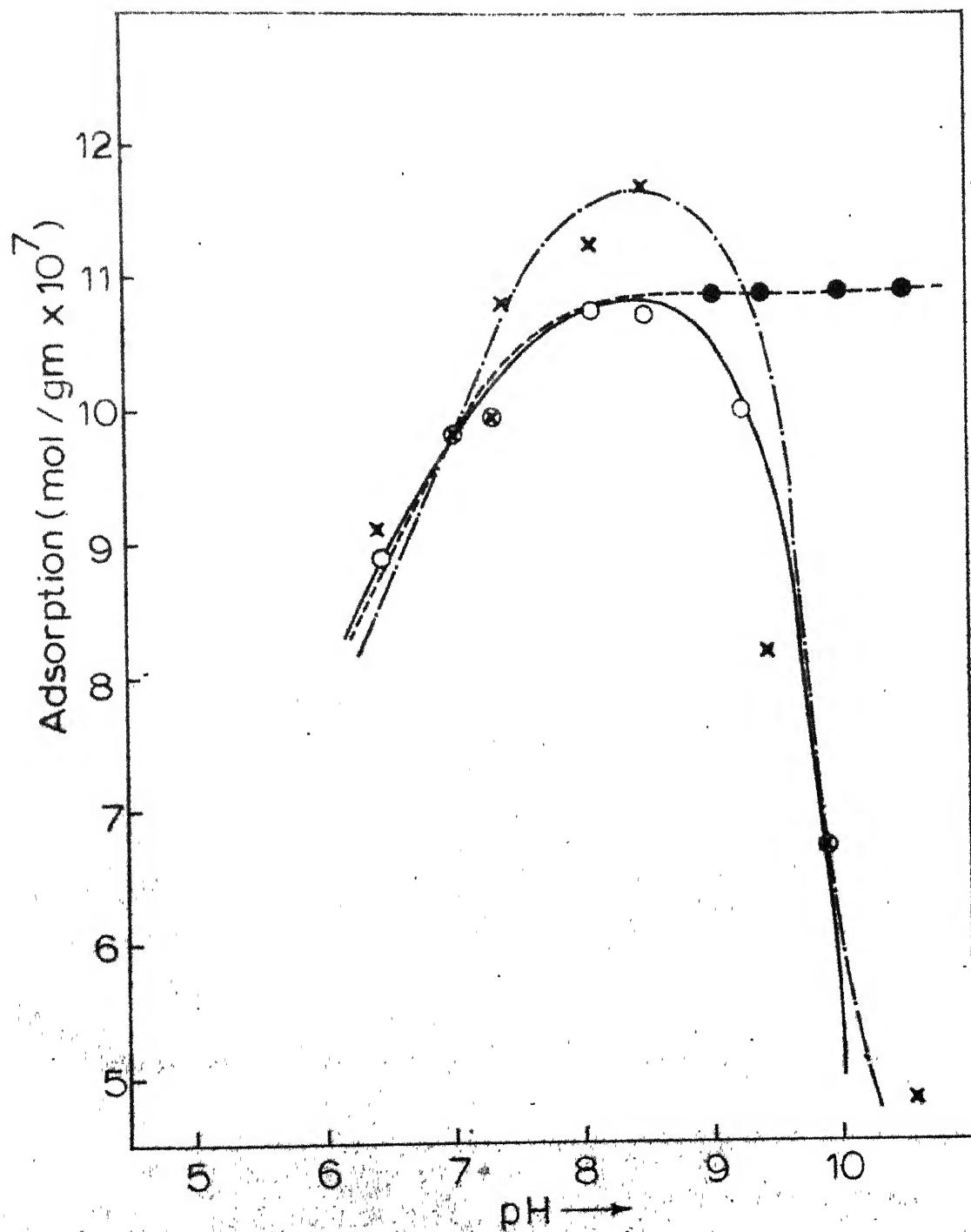
Fig. 16
Zircon-Na-Oleate
Variation of Adsorption with pH.
Experimental ⎯×⎯

CHAPTER - V

ROLE OF HYDROXYL ION AS A DEPRESSOR AND BARSKY'S LAW

That the hydrogen and hydroxyl ions play an important part in modulating the collecting process in froth flotation is well established. In case of anionic collectors in alkaline region, we have a pronounced effect of the hydroxyl ion concentration. The explanation of this effect in terms of certain theoretical postulate forms the subject matter of this chapter. The analysis has been made in a wider context and does not pertain exclusively to any particular system such as the monazite sand minerals.

5.1   THE BARSKY'S LAW: Wark and Cox(35) studied the role of hydroxyl ion as depressor, and competitor of collector anions with reference to adsorption on to the mineral surface. As pH is increased at a suitable fixed anionic collector concentration in the bulk, flotation recovery increases, reaches a maximum and then falls to zero as is evident from Figure 17. The point in acidic region at which recovery is nil is called 'lower critical pH' and the pH in alkaline range at which recovery is again nil is known as 'upper critical pH'. This upper critical pH, obtainable by noncling conditions of the gas bubble also, increases with the increase in bulk concentration of the anionic collector. When the critical pH is plotted against the collector concentration, a curve such as the one shown in Figure 18, is obtained. It is called a 'contact curve' and is frequently used in the depression studies. From the figure it is seen that a contact curve is one which separates the region where flotation is
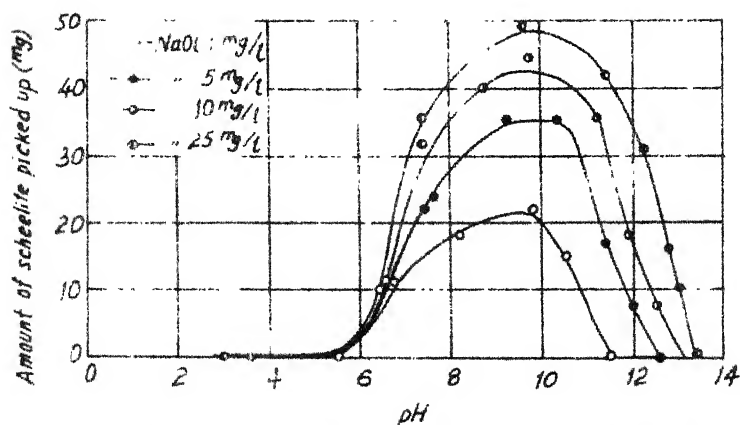
Fig. 17 - Flotation curves for scheelite in solutions of various concentrations of sodium oleate. (S. Mukai)
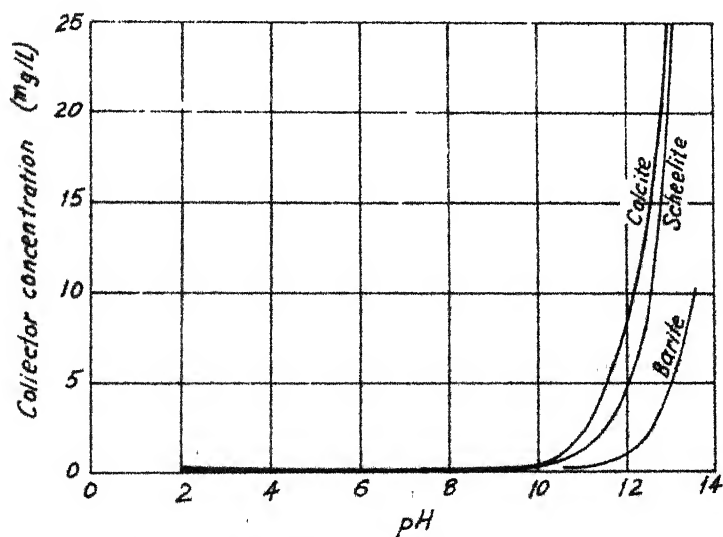
Fig. 18 - Critical contact curves for various non-sulphide minerals, using sodium oleate as collector. (S. Mukai)
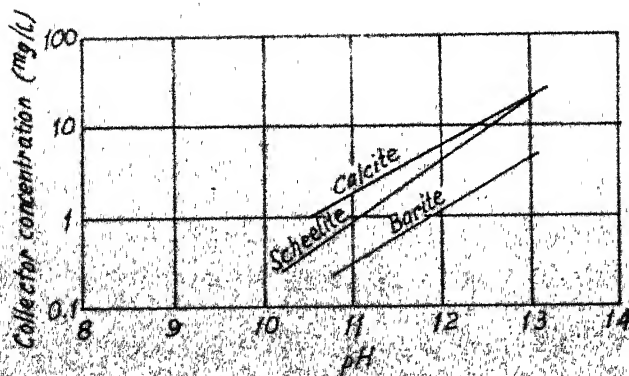
Fig. 19 - Relation between concentration of sodium oleate

possible from the region of nonflotation.

Based on the studies of Wark and Cox, Barsky(36) suggested a generalisation that on a collector concentration -pH diagram, the contact curve separating the flotation and nonflotation zones can be represented by a line along which

$$\frac{C_{L_{X^-}}}{C_{L_{OH^-}}} = \text{constant} = K_b \qquad \ldots \quad (5.1)$$

where $C_{L_{X^-}}$ represents the collector ion concentration and $C_{L_{OH^-}}$ the hydroxyl ion concentration in the bulk of the solution.

According to this postulate, a plot of the logarithm of the collector ion concentration versus the logarithm of hydroxyl ion concentration (or pOH) should be a straight line of unit slope. However, the experimental results of Wark and Cox(35) do not give a slope of unity, though the straight line relationship is observed. Experiments performed by many workers on various mineral-anionic collector systems showed similar behaviour with slopes less than unity. Some of the experimental slopes obtained in different cases are presented in Table 11.

A logical modification of the Barsky's relationship on the basis of these results, as suggested by A.M. Gaudin(40), would be to express it as

$$\frac{C_{L_{X^-}}}{(C_{L_{OH^-}})^m} = \text{constant} = K_b \qquad \ldots \quad (5.2)$$

so that log-log plot would give a slope which need not be unity. Data obtained by Kakovsky(38) on galena-Xanthate and galena-diethyldithiophosphate systems, however, tend to substantiate

TABLE 11

Experimental Barsky Slopes for Various Systems

Mineral	Collector	Experimental Slope (m)	Constant (K_b)	Reference
Galena	Xanthate	0.65	-	(35)
Galena	Sodiumdithio phosphate	0.52	-	(35)
Barite	Sodiumdodecyl benzene sulfonate	0.19	$10^{-1.2}$	(37)
Calcite	- do -	0.39	$10^{0.24}$	(37)
Wolframite	- do -	0.20	$10^{-2.5}$	(37)
Barite	Sodium oleate	0.57	$10^{-4.3}$	(37)
Calcite	- do -	0.49	$10^{-3.7}$	(37)
Scheelite	- do -	0.68	$10^{-3.5}$	(37)
Wolframite	- do -	0.53	$10^{-1.9}$	(37)
Galena	Xanthate	1.00	10	(38)
Galena	dibutyldithio phosphate	1.00	-	(38)
Sphalerite	diethyldithio carbamate	0.56	-	(35)
- do -	dibutyldithio carbamate	0.72	-	(35)
- do -	diamyldithio carbamate	0.75	-	(35)
Chalcopyrite	Na diethyldithio phosphate	0.6	-	(35)
Siderite	Heptylate	0.3	-	(39)

the original statement of the Barsky's law (m = 1).

A.M. Gaudin(40) while summing up the whole situation, stated in 1957 "In case of anionic collectors there is a qualitative relationship of collector ion concentration to hydroxyl ion concentration but to date the existence of a quantitative proportionality of $c_{L_{X^-}}$ to $c_{L_{OH^-}}$ for the establishment of the noncling condition is not proved. In fact it may be said to have been disproved--". However, he feels that the deviation from the original Barsky's relationship may be due to the experimental conditions of variable total electrolyte concentration. This has an appreciable effect on the structure of the double layer. It is to be hoped, therefore, that by keeping total ionic concentration constant Barsky's relationship may be more nearly obtained.

A few studies have been made to justify the Barsky's law and to show the reasons for occasional deviations. These studies can be roughly divided into two subgroups.

1) Predominantly mechanistic approaches

2) Approaches based on properties of the interfaces involved.

5.2 <u>MECHANISTIC APPROACHES</u>:   The basic idea underlying all these approaches is to assign to OH⁻ ion the role of a competitor to the collector anion for being adsorbed on to the mineral surface. Different mechanisms have been proposed to explain this competitive adsorption of OH⁻ and collector anions.

1) Single Site Free Molecule Adsorption:- In this type of mechanism which was advocated by Cook and Wadsworth(41) the molecules and not ions get adsorbed on the mineral surface. The site of the mineral molecule is taken as a single site.

For example:

$$\begin{matrix} Pb \\ | \\ S \\ \text{Galena} \end{matrix} \quad or \quad \begin{matrix} S'' \\ | \\ S' \end{matrix} \qquad \text{is taken as a single site}$$
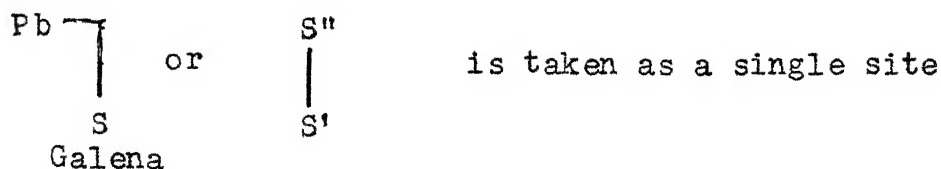
and the collector (say fatty acid) reacts as shown below:

$$HX \; + \; \begin{matrix} -S'' \\ | \\ -S' \end{matrix} \longrightarrow \begin{matrix} HS'' \\ | \\ XS' \end{matrix}$$
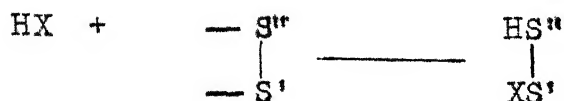
There is not much support to free molecule adsorption as it has
to be physical in nature(40).

2) Double Site - Ion Pair Adsorption:- This mechanism
was forwarded and supported by K.L. Sutherland(42). In this
mechanism separate adsorption sites are supposed to be available
for anions and cations and the adsorption takes place as follows:

$$S' \; + \; H^+ \longrightarrow S' H$$
$$S'' \; + \; X^- \longrightarrow S'' X$$
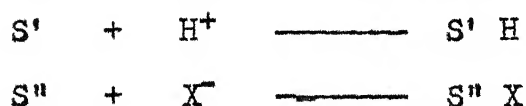
The main objection against this type of adsorption is that since
there is no rule as to the number of S' and S'' the problem
of maintaining charge neutrality arises. Further, Cook et.al(41)
have shown that if treated in details this model leads to
inconsistency.

3) Ionic Adsorption on a Single Site:- In this type of
mechanism which was supported by Wark and Gaudin(40) and many
others, a site M^+ is supposed to be available for the adsorption
of the anions and when they get adsorbed the charge neutrality
is automatically maintained.

$$M^+ \; + \; X^- \longrightarrow M X$$

This also implies that if there are two types of negative ions,
say OH^- and collector anion there will be a competition for

the adsorption site among them. Objection to this mechanism again comes from Cook(41) who has shown that if the above mechanism is taken then the adsorption potential of OH- ions becomes much larger. Since mineral surfaces are easily wetted large values of adsorption potential are rather unexpected.

5.3 APPROACHES BASED ON THE PROPERTIES OF THE INTERFACES: Several studies have been made to visualise the problem in terms of different properties of the interfaces and the condition for critical pH.

1) Surface Chemical Equilibrium:- This approach has been follwed by Kakovsky(38) and many others and is most popular. It assumes that the law of chemical equilibrium is valid for the surface chemical reactions and hence for a reaction of the type

$$M \ OH_X + X^{-z} = M \ OH_{(x-z)}X + z \ OH^-$$
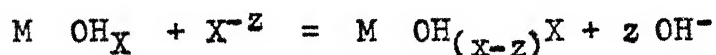
the equilibrium condition can be written as

$$K_o = \frac{\boxed{\ X^- \ }}{\boxed{\ OH^- \ }^z}$$

which is nothing but Barsky's law. In another form the condition can be put as

$$pH = 1/z \ \log \ \boxed{\ X^- \ } \ -1/z \ \log K_o + 14$$

or

$$pH = 1/z \ \log \ \boxed{\ X^- \ } + K_c \qquad \qquad \dots \quad (5.3)$$

where $K_c = 14 -1/z \ \log K_o$ and z is the valency of the collector anions. The above equation suggests a slope of unity in Barsky's plot for univalent collector ions ($z = 1$). Experimental results do not corroborate this expectation.

2) Chemical Affinity Approach:- Paneth and Horovitz(43) concluded on the basis of their adsorption studies that an electrolyte ion tends to be strongly adsorbed on a crystalline

solid if it forms difficultly soluble or weakly dissociated compound with oppositely charged ion of the crystal lattice, i.e., the adsorption depends on the solubility product of the reaction products and subsequently on chemical affinity. Following these observations S. Mukai et.al(44) tried to explain the critical phenomena on the basis of chemical affinities of the X^- (in this case Xanthate), the collector anion and OH^- ion with the cation at the sulfide mineral lattice.

Thus considering the reactions

$$M^{++} + 2X^- \rightleftharpoons MX_2 \quad - \triangle F_I$$

and $\quad M^{++} + 2OH^- \rightleftharpoons M(OH)_2 - \triangle F_{II}$
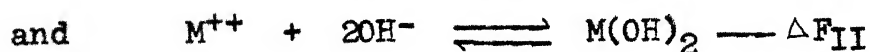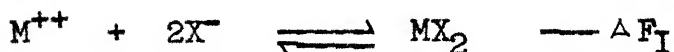
the authors give the critical condition as

$$\triangle F_I = \triangle F_{II} \qquad \qquad \dots \quad (5.4)$$

where

$$\triangle F_I = RT\ln 10 \ \lfloor \log L_{MX_2} + \log 10^{-9} - \log C_{M^{++}} - 2\log C_{X^-} \rfloor$$

$$\dots \quad (5.5)$$

and

$$\triangle F_{II} = RT\ln 10 \ \lfloor \log L_{MOH_2} + \log 10^{-9} - \log C_{M^{++}} - 2\log C_{OH^-} \rfloor (5.6)$$

In the above equations L_{MX_2} and L_{MOH_2} are solubility products of the surface compounds MX_2 and MOH_2 at the surface respectively.

The above condition is nothing but the one obtained by the surface chemical equilibrium considerations, and suffers from similar limitations as stated earlier.

3) Electrochemical Approach:- S. Mukai and T. Wakamatsu(45 observe on the basis of their electrochemical studies on flotation systems that flotation reagents react on the surface of the mineral

as a redox reaction accompanying electron transfer at the solid liquid interface and that the electrode potential is closely correlative with the flotability of the sulfide minerals pyrite and galena.

The relationship between electrode potential and ion concentration is given by the Nernst's equation

$$E = E_0 + RT/nF \ \ln a \qquad \ldots \quad (5.7)$$

where a is the activity of the ion in question. The above equation can also be written as

$$E = P + Q \log C \qquad \ldots \quad (5.8)$$

where P and Q are some other constants and C is the concentration. Figure 20 depicts the variation of the electrode potential with pH at different collector concentrations. The straight line I in the figure shows the behaviour shown without the addition of the Xanthate collector. Thus the change of electrode potential of pyrite by varying pH value of the solution in which absolutely no Xanthate is present can be represented by a linear function

$$E_1 = b_1 \ pH + a_1 \qquad \ldots \quad (5.9)$$

Similarly the relation between the electrode potential of pyrite and concentration of Xanthate collector is expressed on the basis of experimental observations as

$$E = a + b \log C_{X^-} \qquad \ldots \quad (5.10)$$

Now, in figure 20, the curves representing the effect of pH on electrode potential with constant Xanthate addition merge into the line which shows the effect of OH^- ions only. The authors, therefore, state the condition for critical pH as

$$E_1 = E$$
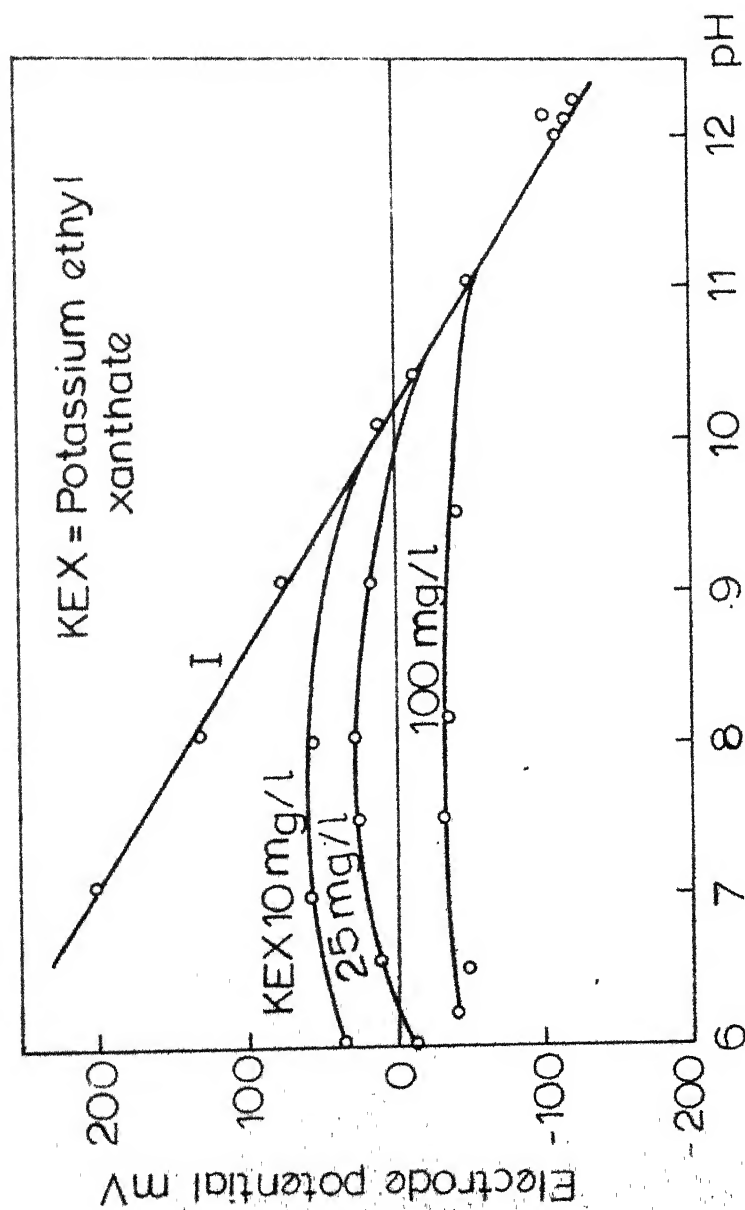
Fig.20-Relation between electrode potential of pyrite and pH at various concentration of potassium ethyl xanthate(KEX).(S.Mukai)

or

$$b_1 \; pH \; + \; a_1 \; = \; a \; + \; b \; \log C_{X^-} \qquad \ldots \quad (5.11)$$

which on further simplification yields

$$\frac{C_{X^-}}{\underline{/}^- C_{OH^-} \underline{}^{\, b_1/b}} \; = \; \frac{a_1 - a - b \log K_w}{b} \qquad \ldots \quad (5.12)$$

where K_w is dissociation constant of water.

Equivalence of Electrochemical and Chemical Equilibrium

Approach:- Presently, it is shown that the equation (5.12) is identical with equation (5.3) derived on the basis of chemical equilibrium considerations provided equations (5.9) and (5.10) are represented in corresponding Nernst forms.

Eqn. (5.9) in corresponding Nernst's form will be

$$E_1 \; = \; E_o \; (OH^-) \; + \; RT/F \; \ln C_{OH^-} \qquad \ldots \quad (5.13$$

where the following reaction is supposed to take place

$$M + OH^- \; \underline{} \; MOH + e^- \qquad \ldots \quad (\; a'$$

Similarly eqn. (5.10) would assume the form

$$E \; = \; E_o \; (X^-) \; + \; RT/F \; \ln C_{X^-} \qquad \ldots \quad (5.14$$

where the supposed electron transfer reaction is

$$M \; + \; X^- \; \underline{} \; MX + e^- \qquad \ldots \quad (\; b'$$

We have

$$E_o \; (OH^-) \; = \; RT/F \; \ln K_c \qquad \ldots \quad (5.15$$

and

$$E_o \; (X^-) \; = \; RT/F \; \ln K_c' \qquad \ldots \quad (5.16$$

respectively, equating E_1 and E and simplifying we get

$$\log \; K_c \; / \; K_c' \; = \; \log C_{X^-} \; - \log C_{OH^-} \qquad \ldots \quad (5.17)$$

or

$$pH \; = \; \log C_{X^-} \; + \; 14 \; - \log \; K_c / K_c' \qquad \ldots \quad (5.18)$$

Now combining reactions (a') and (b') suitably we get overall reaction with equilibrium constant $K_o = K_c \; / K_c'$. Hence the eqn. (5.18) reduces to

$$pH \; = \; \log C_{X^-} \; + \; 14 \; - \log K_o$$

which is eqn. (5.3) with $z = 1$.

It is, therefore, clear that this approach need not be considered separately.

4) Adsorption Approach:- S. Mukai, G. Kano and T. Wakamatsu(46) discussed theoretically the adsorption of X^- and OH^- ion on to the same mineral site. They distinguish between two cases (i) adsorption on the uniform surface and (ii) adsorption on non-uniform surface. One of the implications of this approach is that the slope of the log-log plot as predicted by this approach is unity for uniform surfaces while it is different in case of non-uniform surfaces. This is not borne out by experimental results.

It is thus necessary to investigate the surface chemical equilibrium approach in somewhat more details. The approach requires some sort of a reaction to be assumed.

5.4 DISPLACEMENT AND ION EXCHANGE TYPE MECHANISM: To avoid the objections raised in connection with the previous mechanisms it may be assumed that MOH is already formed due to hydrolysis of the mineral surface. There is ample evidence to show that mineral

surfaces under aqueous solutions are easily hydrolysed(47). Thus the collector ion gets adsorbed by displacing OH^- ions and the following heterogeneous displacement reaction could be suggested.

$$M-OH + X_S^- \rightleftharpoons M-X + OH_S^-$$

Alternatively,

$$M-X + OH_S^- \rightleftharpoons M-OH + X_S^- \qquad \dots \quad (a)$$
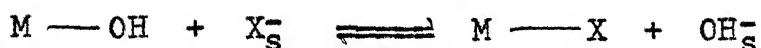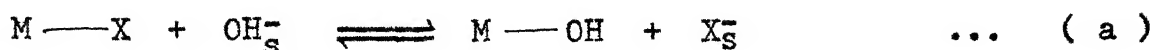
which does not differ in essence from the ion exchange type reaction

$$S-X^- + OH_S^- \rightleftharpoons S-OH^- + X_S^- \qquad \dots \quad (b)$$
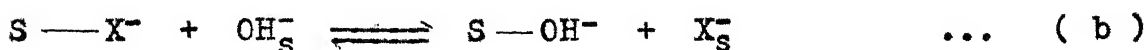
where M and S denote mineral cation and mineral surface respectively. We can ignore the subtle difference between reactions (a) and (b) since adsorption need not correspond to formation of specific stoichiometric compounds in the solid phase. It is, therefore, safe to assign the above as 'ion displacement reaction'.

5.5 <u>CRITICAL APPRECIATION OF THE EQUILIBRIUM APPROACH</u>: In most of the studies made on the basis of this approach(37,38) surface concentrations and bulk concentrations are not clearly defined or differentiated and though the condition refers to surface equilibrium bulk concentrations are freely used. The $\diagup\hspace{-6pt}\diagdown$ symbol in eqn. (5.3) is used to denote unspecified concentrations. It is, therefore, necessary to restate the condition in clear terms.

For a reaction of the type (b) in section 5.4 we can write

$$a_{S_{OH^-}} \cdot a_{L_{X^-}} = K_o' \, a_{S_{X^-}} \cdot a_{L_{OH^-}}$$

or

$$\frac{c_{L_{X^-}}}{c_{L_{OH^-}}} = K_o' \, \frac{c_{S_{X^-}}}{c_{S_{OH^-}}} \, \frac{f_{S_{X^-}} \cdot f_{L_{OH^-}}}{f_{S_{OH^-}} \cdot f_{L_{X^-}}} \qquad \dots \quad (5.19)$$

where a, C, f are activity, concentration and activity
coefficient terms respectively. L and S indicate liquid
bulk phase and solid surface. We may assume f_S values to
be constant and for constant or varying total ionic concentrations
$\frac{f_{LOH^-}}{f_{LX^-}}$ to be constant also.

Therefore (5.19) can be rewritten as follows

$$\frac{C_{L_{X^-}}}{C_{L_{OH^-}}} = K_o' \ \frac{C_{S_{X^-}}}{C_{S_{OH^-}}} \qquad \ldots \quad (5.20)$$

Now, the original statement of the Barsky's law can be claimed
to be valid from (5.20) only if $\frac{C_{S_{X^-}}}{C_{S_{OH^-}}}$ is constant. This is
possible if $C_{S_{X^-}}$ is constant and $C_{S_{OH^-}}$ is so large that its
variation can be neglected. O. Mellegren[48] showed in the case
of ethyl Xanthate-pyrite system that Xanthate adsorption density
($C_{S_{X^-}}$) is singularly dependent on $C_{L_{X^-}} / C_{L_{OH^-}}$ so long as this
ratio is small (< 1). From this, it may be tempting to suggest
that critical contact curve corresponds to constancy of $C_{S_{X^-}}$ and
hence of $C_{L_{X^-}} / C_{L_{OH^-}}$.

Also eqn. (5.3) suggests that when the valencies of the
anions (e.g., OH^- and X^-) are the same the slope m should be
unity. However, this is not corroborated by the experiments as
is clear from Table 11.

As a matter of fact, C_S should increase as C_L is
increased for any of the ionic species, particularly when the
concentrations of other ions remain constant or the system
contains excess neutral electrolyte which ensures constancy of
activity coefficient values. In such instances we may write

If it could be shown that the above equation is valid for all oleate ion concentrations, and the flotation / no flotation transitional points are characterised by constant adsorption magnitude of oleate ion, then modified Barsky's law would be established.

To summarise, deviation of the value of m from unity cannot be explained in terms conventional chemical or electrochemical equilibrium approach. For flotation/no flotation transition, (i) constancy of C_{SX^-} or (ii) constancy of $C_{SX^-} / (C_{SOH^-})^{m'}$, if experimentally proven, would substantiate modified Barsky's law. Case (ii), however, has no theoretical significance.

It may be necessary to base the arguments on some more fundamental parameter such as the surface free energy.

5.6 SURFACE FREE ENERGY HYPOTHESIS: It is proposed that in order to have a three phase contact the specific surface free energy (ν) of the solid interface must be lowered by some minimum magnitude ($d\nu$) and this would correspond to critical contact curve in the collector concentration-pH plot. Other constant contact angle curves, parallel to the critical contact curve would represent higher values of $d\nu$, i.e., lower values of ν.

For a number of adsorbable species, Gibb's adsorption equation postulates

$$(d\nu)_{P,T} = -\sum \Gamma_i d\mu_i \qquad \ldots \quad (5.22)$$

where Γ_i and μ_i stand for surface excess and chemical potential of the ith component respectively. Assuming that total ionic concentration is constant and concentrations of other adsorbable ions except X^- and OH^- do not change, we may write

$$(d\nu) = -\Gamma_{X^-} d\mu_{X^-} - \Gamma_{OH^-} d\mu_{OH^-} \qquad \ldots \quad (5.23$$

The reference point corresponds to zero aqueous concentration of X^- and OH^-. It is also evident that Γ_{OH^-} is negative since Γ_{X^-} is positive; only this shall ensure constancy of $d\nu$ when C_{OH^-} and C_{X^-} in the aqueous phase go on increasing.

The adsorption isotherms of species X^- and OH^- at a particular temperature may be represented by

$$\Gamma_{X^-} = K_1 \, C_{X^-}^{p} \quad \text{and} \quad \Gamma_{OH^-} = -K_2 \, C_{OH^-}^{q} \qquad \ldots \quad (5.24)$$

For a three-phase contact, much less than a monolayer adsorption of the collector is needed, and the required magnitude of $d\nu$ is relatively small. Now, as aqueous concentrations of X^- and OH^- go on increasing, the magnitude of $d\nu_{X^-}$ (due to X^-, negative in sign) and $d\nu_{OH^-}$ (due to OH^-, positive sign) go on increasing, the summation (i.e., the difference between the magnitudes) remaining constant, along the critical contact curve.

$$\left| d\nu_{X^-} \right| \quad - \quad \left| d\nu_{OH^-} \right| \quad = \quad - d\nu \quad \ldots \quad (5.25)$$

Since the left hand side terms in eqn. (5.25) would be increasingly larger compared to their constant difference, we can approximate that

$$\left| d\nu_{X^-} \right| \quad \approx \quad \left| d\nu_{OH^-} \right|$$

and equality may be assumed when C_{X^-} and C_{OH^-} are reasonably large.

Then we shall write,

$$\Gamma_{X^-} \, d\mu_{X^-} \quad = \quad \Gamma_{OH^-} \, d\mu_{OH^-}$$

or

$$RT \int_{0}^{C_{X^-}} K_1 \cdot C_{X^-}^{p-1} \cdot d\,C_{X^-} = RT \int_{0}^{C_{OH^-}} K_2 \cdot C_{OH^-}^{q-1} \cdot d\,C_{OH^-}$$

Solving, we have for any point on the critical contact

curve

$$K_1' \cdot c_{X-}^{p} = K_2' \, c_{OH-}^{q}$$

or

$$\frac{c_{L_{X-}}}{(c_{L_{OH-}})^{m}} = \text{constant}$$

where $m = q/p$.

It may be noted that this conclusion is similar to what emerged from the assumption that $c_{S_{X-}} / (c_{S_{OH-}})^{m'}$ is constant along the critical contact curve. The implications are also similar.

Ultimately, the validity of the Barksy's law rests on either the constancy of surface adsorption of the collector ion ($c_{S_{X-}}$) or constancy of the surface free energy.

To test the above hypothesis, therefore, accurate determinations of surface adsorption (c_S) and surface excess (Γ) parameters around contact/no contact zone are extremely necessary. Experimental determinations of the above parameters may lead to the conclusion that the flotation / no flotation transitional points denote either constancy of adsorption of the collector or constant surface free energy at the solid liquid interface or both.

Any conclusion of the above nature should help us in predicting the optimum pH value for selective flotation of one mineral in preference to another.

CHAPTER - VI

CONCLUSION

The described work was undertaken to study the flotation and adsorption characteristics of the monazite sand minerals, with sodium oleate as a collector, and to explore any possible interrelationship between the two.

It is concluded on the basis of experimental studies that the flotation and adsorption properties are closely correlative.

The maximum obtained on the flotation and adsorption curves can be explained in terms of increasing oleate ion concentration with pH and competition offered by hydroxyl ion acting as depressor, with respect to adsorption of the collector ion on the solid surface.

A general relationship to explain the shape of the adsorption curves has been worked out and is given by the eqn. (4.10)

The fit obtained on the basis of this equation is reasonably satisfactory.

Feasibility of a more exact fit using somewhat complex expressions is indicated.

Furthermore, the theoretical validity of the Barsky's law is critically examined and it is concluded that postulation of a specific stoichiometric surface reaction is unnecessary and that surface free energy hypothesis lends a better theoretical validity subject to the conditions and assumptions specified.

From the practical point of view it is tentatively suggested that order of flotability of the minerals is zircon $>$ monazite $>$ ilmen

It is also observed that all the minerals are very well flotable by sodium oleate and selective flotation is not possible by using collector alone.

Necessity of a suitable modulating agent is, therefore, obvious and thus, more work in these directions is necessary. Parallel adsorption and flotation studies with respect to monazite sand mineral-collector-depressor systems are likely to yield fruitful results.

APPENDIX A

TABLE 12

Minerological Composition of Beach Sand from

Travancore Belt

Mineral	Beach Washings		Dune Material	
	Kadiapatanam	Chinnavi-lai	Valliar Bank	Chinna-vilai
	%	%	%	%
Ilmenite	75	69	60	60
Garnet	3	7	2	4
Zircon	6	6	5	5
Rutile	4	4	3	4
Monazite	4	2	2	2
Silica & the rest	8	9	28	25
Total	100	100	100	100

$\sqsubset$ Ref: P. Viswanathan: Studies on Travancore Beach Sands.

Indian Mining Journal, Special Issue, 110, (1957) $\_7$

TABLE 13

Typical Sieve Analysis of Manavalakurichi Sands (-28 mesh)

Mesh Tyler		Weight in percent
	+ 35	0.6
- 35	+ 48	12.0
- 48	+ 65	36.0
- 65	+100	40.0
-100	+150	10.0
-150	+200	1.0
-200	+270	0.4

Mining Magazine, 18, 113 (1965) $\_7$

TABLE 14

Minerological Description of the Minerals

Mineral	Chemical Formula	Specific Gravity	Hard-ness	Crystal Structure	Special Features
Zircon	$ZrSiO_4$	4.4 - 4.8	7.5	Tetragonal	Obtained from Florida
Monazite	$(Ce,Dy\ Nd)PO_4$	4.9-5.3	5.5	Monoclinic	Obtained from Travancore
Ilmenite	$FeTiO_3$	4.3 - 5.5	5.6	Hexagonal	Obtained From Travancore

APPENDIX B

TABLE 15

Variation of Zircon Recovery with pH

Collector Conc.n. – 25.6 mg/litre
Frother – 5 c.c. of the solution made by dissolving 5 c.c. of Dowfroth in 100 c.c.
R.P.M. – 600 – for conditioning
1400 – for flotation

S. No.	pH	Percent Recovery
1.	2.48	0.00
2.	2.74	38.86
3.	3.35	57.26
4.	4.50	68.23
5.	4.95	80.93
6.	7.80	90.60
7.	8.40	90.40
8.	10.80	53.14
9.	11.20	31.50

TABLE 16

Variation of Zircon Recovery with pH

Collector Conc.n. – 21.05 mg/litre
Frother – 7 c.c. of the solution made by dissolving 5 c.c. of Dowfroth in 100 c.c.
R.P.M. : 900 – for conditioning
1500 – for flotation

S. No.	pH	Percent Recovery
1.	6.52	78.50
2.	6.62	89.15
3.	7.01	91.62
4.	7.75	94.50
5.	9.70	94.10
6.	10.12	89.97
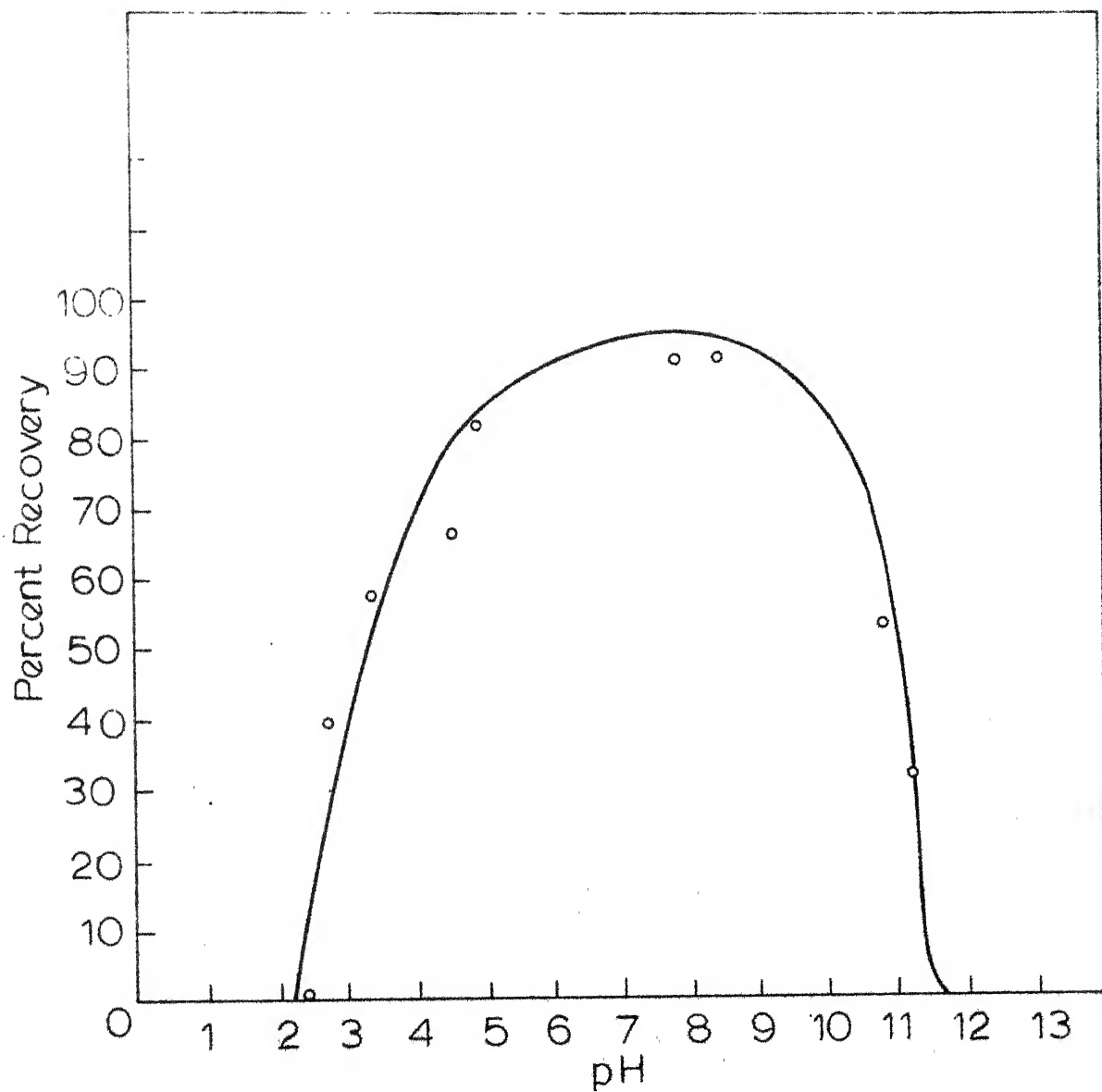
Fig. 21
Zircon - Na - Oleate
pH - Percent Recovery

APPENDIX C

TABLE 17

β-Values for Different Concentrations (49)

S. No.	Molar Concentration (S)	Degree of Hydrolysis	Temperature
1	1.0×10^{-5}	0.0181 0.0322	25 °C 40 °C
2	1.0×10^{-4}	0.0131 0.0238	25 °C 40 °C
3	2.33×10^{-4}	0.0151 0.0271	25 °C 40 °C
4	3.32×10^{-4}	0.0201 0.0301	25 °C 40 °C
5	1.0×10^{-3}	0.0619 0.0702	25 °C 40 °C
6	1.0×10^{-2}	0.0369 0.0476	25 °C 40 °C

TABLE 18

Oleate Ion Concentration for Different pH Values

(gmions/litre)

pH	S= 10^{-3} mol/litre 25 °C	S = 10^{-3} mol/litre 40 °C	S = 10^{-4} mol/litre 40 °C	S=2.33x10^{-4} mol/litre 40 °C	S=3.32x10^{-4} mol/litre 40 °C
1	2.446×10^{-11}	1.88×10^{-11}	4.098×10^{-10}	1.295×10^{-10}	1.064×10^{-10}
2	2.446×10^{-10}	1.88×10^{-10}	4.098×10^{-9}	1.295×10^{-9}	1.064×10^{-9}
3	2.446×10^{-9}	1.88×10^{-9}	4.098×10^{-8}	1.295×10^{-8}	1.064×10^{-8}
4	2.446×10^{-8}	1.88×10^{-8}	4.098×10^{-7}	1.295×10^{-7}	1.064×10^{-7}
5	2.446×10^{-7}	1.88×10^{-7}	3.936×10^{-6}	1.295×10^{-6}	1.064×10^{-6}
6	2.441×10^{-6}	1.88×10^{-6}	2.906×10^{-5}	1.227×10^{-5}	1.030×10^{-5}
7	2.389×10^{-5}	1.85×10^{-5}	8.039×10^{-5}	8.326×10^{-5}	8.054×10^{-5}
8	1.965×10^{-4}	1.58×10^{-4}	9.770×10^{-5}	1.978×10^{-4}	2.530×10^{-4}
9	7.098×10^{-4}	6.53×10^{-4}	9.777×10^{-4}	2.290×10^{-4}	3.221×10^{-4}
10	9.607×10^{-4}	9.50×10^{-4}	1.000×10^{-4}	2.326×10^{-4}	3.310×10^{-4}
11	9.961×10^{-4}	9.99×10^{-4}	1.000×10^{-4}	2.330×10^{-4}	3.320×10^{-4}
12	1.000×10^{-3}	1.00×10^{-3}	1.000×10^{-4}	2.330×10^{-4}	3.320×10^{-4}
13	1.000×10^{-3}	1.00×10^{-3}	1.000×10^{-4}	2.330×10^{-4}	3.320×10^{-4}
14	1.000×10^{-3}	1.00×10^{-3}	1.000×10^{-4}	2.330×10^{-4}	3.320×10^{-4}

APPENDIX D

Derivation of an Expression for Calculating Oleate-Ion

Concentration at any pH above C.M.C.

For the case when $S \gg$ C.M.C. the steps II and III in reaction (a) Section 4.3 are also to be taken into consideration and hence, we have,

$$K_d = \frac{(Ol^-)_m}{(Ol^-)_s} \qquad \text{and} \quad K_F = \frac{(HOl)_m}{(HOl)_s} \qquad \ldots \quad (D.1)$$

Also

$$(Ol^-)_s + (Ol^-)_m = (1-\beta)\ S\ V \qquad)$$
$$)$$
and $\qquad\qquad\qquad\qquad\qquad\qquad\qquad)\qquad \ldots \quad (D.2)$
$$)$$
$$(HOl)_s + (HOl)_m = \beta\ S\ V \qquad\quad)$$

where V- Total volume (say 1 litre). These considerations give the following expression for K_h (50)

$$K_h = \frac{\beta^2\ S\ \rho}{(Ol^-)_s\ K_F} \qquad\qquad \ldots \quad (D.3)$$

where

$$\rho = \frac{10^3}{\text{Mol. wt. of soap}} \qquad\qquad \ldots \quad (D.4)$$

Also the mass balance equation becomes

$$S = (Ol^-)_s + (Ol^-)_m + (HOl)_s + (HOl)_m$$

or using (D.1), we get

$$S = (Ol^-)_s\ (1+ K_d) + (HOl)_s\ (1 + K_F) \qquad \ldots \quad (D.5)$$

Substituting for $(HOl)_s$ from (D.5) in equation 4.1 Chapter IV

we get,

$$K_h = \frac{\dfrac{S - (1+K_d)\,(Ol^-)_s}{(1+K_F)}\,(OH^-)}{(Ol^-)_s}$$

or

$$(Ol^-)_s = \frac{S \cdot (OH^-)}{K_h\,(1+K_F) + (1+K_d)\,(OH^-)} \qquad \dots \quad (D.6)$$

Using equation (D.3), we get,

$$(Ol^-)_s = \frac{S\,(OH-)}{\dfrac{\beta^2\,S\,\varrho\,(1+K_F)}{(Ol-)_s\,K_F} + (OH^-)\,(1+K_d)}$$

Simplifying we get

$$(Ol^-)_s = \frac{S}{1+K_d} - \frac{\beta^2\,S\,\varrho\,(1+K_F)}{K_F(1+K_d)\,10^{(pH-14)}} \qquad \dots \quad (D.7)$$

Thus $(Ol^-)_s$ can be calculated if β, K_F and K_d are known. Also $(HOl)_s$, $(Ol^-)_m$ and $(HOl)_m$ can be subsequently calculated for different pH values. Implicit in the above derivation is the assumption that K_h, K_d, K_F do not change with pH.

APPENDIX E

TABLE 19

Computational Data and Value of the Constants

Mineral	K_1	n_1	K_2	n_2
Ilmenite	2.75×10^{-6}	0.123	1.22×10^{-1}	1.30
Monazite	3.96×10^{-6}	0.170	8.53×10^{-1}	1.50
Zircon	2.85×10^{-6}	0.115	4.50×10^{-2}	1.25

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